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LONG-RANGE ELECTROSTATIC AND ELECTROMAGNETIC INTERACTIONS BETWEEN ATOMS

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16. ABSTRACT

The object of this calculation is to examine the contribution to the interaction energy between two neutral hydrogenic atoms in their ground state because of their electrostatic interaction and the presence of an electromagnetic radiation field in the system. The inclusion of the radiation field in the Hamiltonian of the system gives rise to retardation effects in the interaction energy which are a function of the separation R between the atoms. These effects are unimportant for distances smaller than the wavelength λ, associated with the radiation being considered, and increase in importance as R approaches λ. In the case of atomic systems, the smallest wavelength associated with atomic transitions is large when compared to the atomic dimensions ($\lambda >> a_0$, where a_0 is the Bohr radius); hence, the problem can be treated using nonrelativistic quantum electrodynamics. This allows us to neglect the particle "spin" and to use simple product eigenfunctions for the atomic and photon states. In addition, the above simplifications make it possible to treat the problem using standard nondegenerate perturbation theory. This feature is crucial since the calculation must be pushed to fourth order before obtaining non-zero corrections to the interaction energy due to the radiation field.

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LONG-RANGE ELECTROSTATIC AND ELECTROMAGNETIC INTERACTIONS BETWEEN ATOMS

SUMMARY

The object of this calculation is to examine the contribution to the interaction energy between two neutral hydrogenic atoms in their ground state because of their electrostatic interaction and the presence of an electromagnetic radiation field in its "vacuum" state. The separation distance R between the atoms is large compared to atomic dimensions, and is of the order of the transition wavelength λ associated with the 1s-2p atomic transitions. Thus, the atoms are sufficiently separated so that the overlapping of their respective charge distributions is neglected along with "spin." The problem is then handled using nonrelativistic quantum electrodynamics.

The Hamiltonian of the system consists of the following parts: $H^{(0)}$, which corresponds to the sum of the Hamiltonians of the respective isolated atoms plus the "vacuum" photon state of the radiation field; $H^{(1)}$, which corresponds to the $\vec{A}(\vec{\rho}) \cdot \vec{P}(\vec{\rho})$ type interactions between the atoms and the radiation field through the electromagnetic potential $\vec{A}(\vec{\rho})$; $H^{(2)}$, which corresponds to the $\vec{A}(\vec{\rho}) \cdot \vec{A}(\vec{\rho})$ type interactions between the atoms and the radiation field; and H_q, the electrostatic interaction between the atoms. Stationary state perturbation theory is then used to obtain the interaction energy of the system to fourth order in the electron charge $\underline{e}$. By retaining higher order multipoles (up to octupole orders) in the expansion of H_q and expanding the retardation factor $\left(e^{i\vec{\kappa} \cdot \vec{r}}\right)$ in $\vec{A}(\vec{\rho})$ in a power series, the interaction energy is obtained, accurate to quadrupole-quadrupole orders.

The results are given as corrections to the various electrostatic multipoles corresponding to the dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions between the atoms. The inclusion of the radiation field in the Hamiltonian of the system is found to give rise to retardation effects in the interaction energy which are a function of the separation distance R. The dipole-dipole results are in agreement with the calculations of Casimir and Polder [1] and others. The dipole-quadrupole approximations can be written as a sum of three quantities proportional to R^{-7}, R^{-8}, and R^{-9}. The R^{-8} term corresponds to the purely electrostatic interaction and the others result from the inclusion of the radiation field in

the system. In the limit of large R ($R>>\lambda$), the dipole-quadrupole electrostatic interaction energy (proportional to R^{-8}) is found to be reenforced by a factor proportional to R^{-9} and diminished by a factor proportional to R^{-7}. The results go over into the electrostatic case for small R ($R<<\lambda$), showing that the retardation effects are unimportant for small separations as in the dipole-dipole case. The corrections to the quadrupole-quadrupole electrostatic interaction (proportional to R^{-10}) are much more complex. The resulting expressions consist of terms proportional to R^{-7}, ... R^{-11}. The above results are expressed in terms of integral functions over $b \equiv \kappa R$, where κ is the magnitude of the wave vector $\vec{\kappa}$ associated with the radiation field.

INTRODUCTION

The object of this calculation is to examine the contribution to the interaction energy between two neutral hydrogenic atoms in their ground state because of their electrostatic interaction and the presence of an electromagnetic radiation field in the system. The inclusion of the radiation field in the Hamiltonian of the system gives rise to retardation effects in the interaction energy [1] which are a function of the separation R between the atoms. These effects are unimportant for distances smaller than the wavelength λ, associated with the radiation being considered, and increase in importance as R approaches λ. In the case of atomic systems, the smallest wavelength associated with atomic transitions is large when compared to the atomic dimensions ($\lambda >> a_0$, where a_0 is the Bohr radius); hence, the problem can be treated using nonrelativistic quantum electrodynamics. This allows us to neglect the particle "spin" and to use simple product eigenfunctions for the atomic and photon states. In addition, the above simplifications make it possible to treat the problem using standard nondegenerate perturbation theory. This feature is crucial since the calculation must be pushed to fourth order before obtaining non-zero corrections to the interaction energy due to the radiation field.

This problem was first treated to first order in both the electrostatic interaction potential and the radiation field (dipole-dipole approximation) by Casimir and Polder [1]. These authors used an elegant by asymmetrical method consisting of first treating the interaction between one atom with the radiation field and then considering this distorted field and the second atom as the initial configuration for subsequent approximations. Leech [2] attempted to solve the problem (to first order) in a more systematic manner using nondegenerate perturbation theory. His results were in disagreement with Casimir and Polder, and, later were reported to be in error by Aub, Power and Zienau [3]. Subsequent calculations by Power and Zienau [4] using a different method verified Casimir and Polder's results. They applied straightforward perturbation theory to a reduced interaction Hamiltonian consisting of only the transverse component of the electric field vector. In this reduced Hamiltonian the electrostatic interaction is not given explicitly; hence if the interaction between the electrostatic interaction potential and the electromagnetic potential is desired, this method cannot be used. Subsequent calculations [5] using field theoretic techniques have since established the correctness of Casimir and Polder's results.

In this calculation the Casimir and Polder results are verified, using a systematic application of nondegenerate perturbation theory and a conventional expression for the interaction Hamiltonian. The calculations are extended beyond the dipole approximations of Casimir and Polder, by including terms up to octupole order in the electrostatic potential, in order to obtain interaction energies accurate [6] to quadrupole-quadrupole orders, and by retaining the first five terms in a power series expansion of the retardation factor of the electromagnetic potential. In this way, corrections due to the radiation field are obtained for each of the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole electrostatic interaction energies. In addition, a systematic analysis is performed to determine how the electrostatic interaction potential is coupled with the electromagnetic potential to produce the retardation effects to the electrostatic interaction energy of the system.

FORMULATION OF THE HAMILTONIAN

Consider a system of two one-electron neutral atoms separated by a large distance R, ($R >> a_0$, where a_0 is the Bohr radius), interacting through their electrostatic potential H_q in the presence of a radiation field described by an electromagnetic potential $\vec{A}(\vec{\rho})$. In addition, assume the respective nuclei to be at rest (Born-Oppenheimer Approximation) and neglect all "spin" interactions between particles. The Hamiltonian for this system is then given by

$$H = H_I + H_{II} + H_q + H_r \quad ; \tag{1}$$

where H_I and H_{II} are the Hamiltonians for atoms I and II, given by

$$H_I = \frac{1}{2\mu}\left(\vec{P}_I - \frac{e}{c}\vec{A}_I\right)^2 - \frac{e^2 Z_I}{|\vec{r}_1|} \quad . \tag{2}$$

H_q is the electrostatic potential [6] between the two charge distributions defined in a coordinate system such that $\vec{R}$ is along the Z axis (Fig. 1) and given by

$$H_q = \sum_{L_1=1}^{\infty} \sum_{L_2=1}^{\infty} \frac{(-1)^{L_2} r_1^{L_1} r_2^{L_2}}{R^{L_1+L_2+1}} \frac{4\pi e^2 (L_1+L_2)!}{\left[(2L_1+1)(2L_2+1)\right]^{1/2}}$$

$$\times \sum_{M=-L_<}^{M=+L_<} \frac{Y_{L_1}^{M^*}(\theta_1,\phi_1)\, Y_{L_2}^{-M^*}(\theta_2,\phi_2)}{\left[(L_1+M)!\,(L_1-M)!\,(L_2-M)!\,(L_2+M)!\right]^{1/2}} \quad . \tag{3}$$

H_r is the electromagnetic field Hamiltonian given by

$$H_r = \sum_{\kappa \gtrless 0} \sum_{\lambda=1}^{2} \hbar c \kappa\, \mathfrak{a}_\lambda^+(\vec{\kappa})\, \mathfrak{a}_\lambda(\vec{\kappa}) \quad . \tag{4}$$

The creation and destruction operators $\mathfrak{a}_\lambda^+(\vec{\kappa})$ and $\mathfrak{a}_\lambda(\vec{\kappa})$ are defined through the quantized vector potential[1] $\vec{A}(\vec{\rho})$ given by

$$\vec{A}(\vec{\rho}) = \frac{c}{i}\sqrt{\frac{2\pi\hbar}{\text{Vol.}}} \sum_{\kappa \gtrless 0} \left(\frac{1}{c\kappa}\right)^{1/2} \sum_{\lambda=1}^{2} \left\{\mathfrak{a}_\lambda(\vec{\kappa})\, e^{i\vec{\kappa}\cdot\vec{\rho}} - \mathfrak{a}_\lambda^+(\vec{\kappa})\, e^{-i\vec{\kappa}\cdot\vec{\rho}}\right\} \hat{\epsilon}_\lambda(\vec{\kappa}) \quad . \tag{5}$$

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1. See Heitler's Quantum Theory of Radiation for the definition of the various quantities in $\vec{A}(\vec{\rho})$.

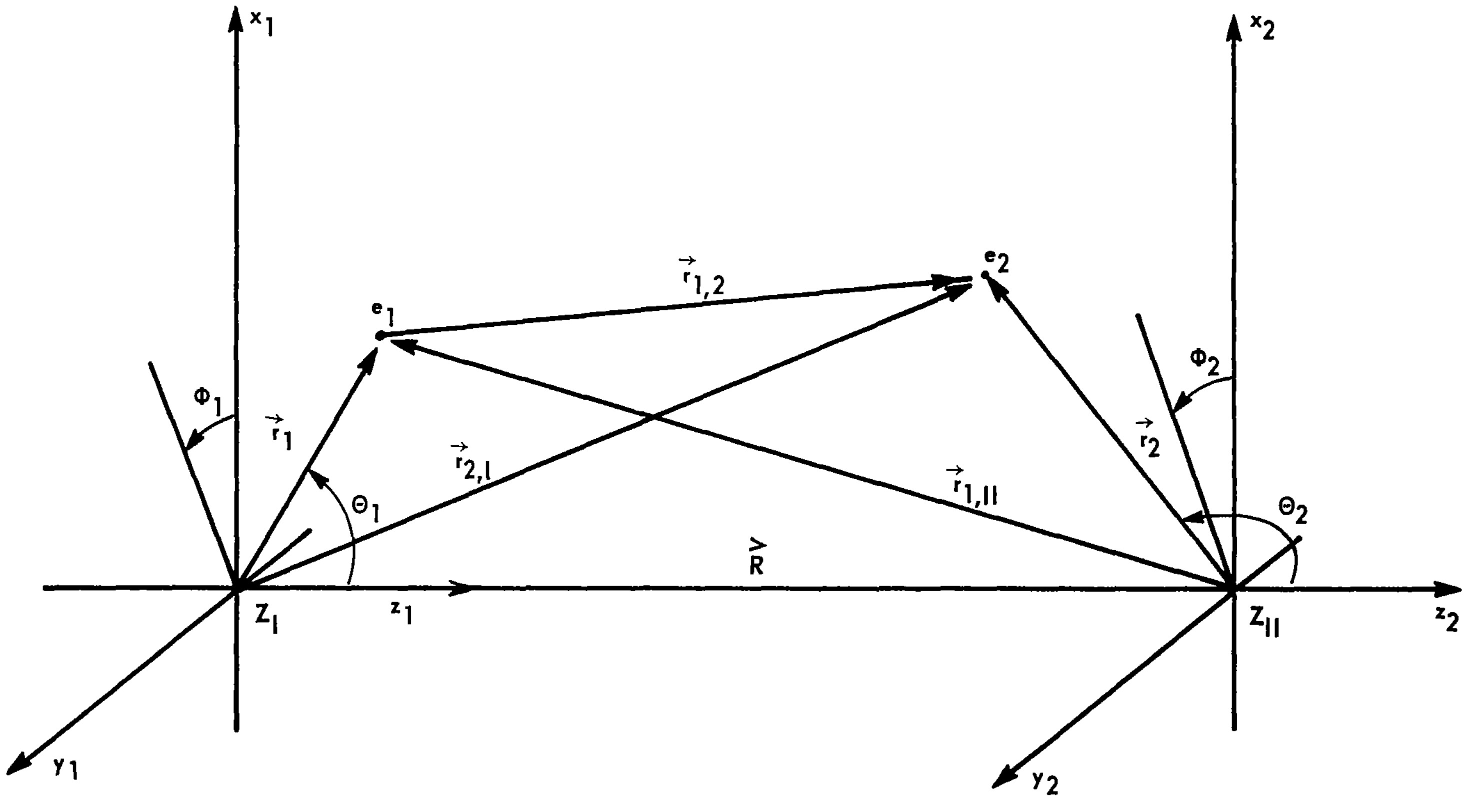


Figure 1. System coordinates.

Expanding equation (2), one obtains

$$H_I = \left\{ \frac{\vec{P}_I \cdot \vec{P}_I}{2\mu} - \frac{e^2 Z_I}{|\vec{r}_1|} \right\} - \frac{e}{2\mu c}\left(\vec{A}_I \cdot \vec{P}_I + \vec{P}_I \cdot \vec{A}_I \right) + \frac{e^2}{2\mu c^2} \vec{A} \cdot \vec{A} \quad , \tag{6}$$

where the first term in braces is just the unperturbed Hamiltonian for a single atom. If one defines the terms in equations (3) and (6) as follows:

$$H_I^{(0)} \equiv \left(\frac{\vec{P}_I \cdot \vec{P}_I}{2\mu} - \frac{e^2 Z_I}{|\vec{r}_1|} \right) \quad , \tag{7}$$

$$e\, H_I^{(1)} \equiv \frac{-e}{2\mu c}\left(\vec{A}_I \cdot \vec{P}_I + \vec{P}_I \cdot \vec{A}_I \right) \quad , \tag{8}$$

$$e^2\, H_I^{(2)} \equiv \frac{e^2}{2\mu c^2}\left(\vec{A}_I \cdot \vec{A}_I \right) \quad , \tag{9}$$

$$e^2\, H_q^{(2)} \equiv H_q \quad , \tag{10}$$

then the total Hamiltonian given by equation (1) may be written as

$$H = H_I^{(0)} + H_{II}^{(0)} + e\left(H_I^{(1)} + H_{II}^{(1)} \right) + e^2\left(H_I^{(2)} + H_{II}^{(2)} + H_q^{(2)} \right) + H_r \ .$$

Further simplification is accomplished by considering the fact that the radiation field Hamiltonian, as given by equation (4), has as eigenvalues the number of photons present in any given state. Thus, if one picks the vacuum state defined by $|, 0, 0, \ldots >$ as the ground state of the radiation field, there are no photons interacting with the atoms in the ground state, and H_r may be written as $H_r^{(0)}$ and combined with $H_I^{(0)}$ in equation (7). Incorporating this modification in the above expression, the total Hamiltonian may be defined as

$$H = \left(H_I^{(0} + H_{II}^{(0)} + H_r^{(0)} \right) + e \left(H_I^{(1)} + H_{II}^{(1)} \right) + e^2\left(H_I^{(2)} + H_{II}^{(2)} + H_q^{(2)} \right). \tag{11}$$

If one further redefines the preceding quantities as follows,

$$H^{(0)} \equiv \left(H_I^{(0)} + H_{II}^{(0)} + H_r^{(0)}\right) \quad , \tag{12}$$

$$H^{(1)} \equiv \left(H_I^{(1)} + H_{II}^{(1)}\right) \quad , \tag{13}$$

$$H^{(2)} \equiv \left(H_I^{(2)} + H_{II}^{(2)} + H_q^{(2)}\right) \quad , \tag{14}$$

one may use perturbation theory techniques to solve the problem by considering the total Hamiltonian as a series expansion in powers of the electron charge $\underline{e}$ given by

$$H = e^0 H^{(0)} + e^1 H^{(1)} + e^2 H^{(2)} \quad . \tag{15}$$

EIGENFUNCTIONS AND EIGENVALUES

System Eigenfunctions

A systematic study of the interaction between two atoms requires the knowledge of their respective states given in terms of eigenfunctions of the system. When perturbation theory is used to treat a given problem, the unperturbed state eigenfunctions must be determined completely[2].

In this problem, it will be assumed that the atoms of the system are sufficiently separated so that the overlapping of their respective charge distributions can be neglected. In this case, the unperturbed nth state of the system can be expressed as products of eigenfunctions given by

$$\psi^{(0)}_{n,(N)} \equiv \psi^{(0)}_n(\mathrm{I})\, \psi^{(0)}_n(\mathrm{II})\, \psi^{(0)}_{(N)}(r) \quad . \tag{16}$$

---

2. This state is sometimes referred to as the ground state of the system.

If one examines the system such that the unperturbed state corresponds to the ground state, then equation (16) is replaced by

$$\psi^{(0)}_{1,(0)} = \psi^{(0)}_{1}(\mathrm{I})\,\psi^{(0)}_{1}(\mathrm{II})\,\psi^{(0)}_{(0)}(r) \quad , \tag{17}$$

where $\psi^{(0)}_{1}(\mathrm{I})$ represents the unperturbed eigenfunction for atom I in its lowest state, and $\psi^{(0)}_{(0)}(r)$ represents the state of the radiation field in its ground state (sometimes referred to as the "vacuum" state). Since hydrogenic eigenfunctions are used for the atomic states, and the electromagnetic potential is expressed in terms of creation and destruction operators $\mathfrak{a}^{+}_{\lambda}(\vec{\kappa})$, $\mathfrak{a}_{\lambda}(\vec{\kappa})$, alternate definitions for the eigenfunctions given in equation (16) are necessary. Let us define $\psi^{(0)}_{n,(N)}$ as follows:

$$\psi^{(0)}_{n,(N)} \equiv \left|,\ldots N_{\lambda}(\vec{\kappa}),\ldots\right\rangle \left|\mathrm{I}(n)\,\mathrm{II}(n)\right\rangle \quad , \tag{18}$$

$$\psi^{(0)}_{\alpha} \equiv \left|,\ldots N_{\lambda}(\vec{\kappa}),\ldots\right\rangle \left|\mathrm{I}(n,\ell,m)\ \mathrm{II}(n,\ell,m)\right\rangle \quad . \tag{19}$$

If one wishes to express an intermediate state in which atoms I and II are not necessarily in the same state, and the photon state contains more than one photon having different parameters κ,λ then one denotes this state by

$$\psi_{\alpha'} \equiv \left|,\ldots N_{\lambda}(\vec{\kappa}),\ldots N'_{\lambda'}(\vec{\kappa}'),\ldots\right\rangle \left|\mathrm{I}(n)\ \mathrm{II}(m)\right\rangle \quad , \tag{20}$$

where atom I is found in the state having quantum numbers n; atom II has quantum number m; the photon state contains N photons having parameters κ,λ; and N' photons with parameters κ',λ'.

The hydrogenic eigenfunctions are defined by [7]

$$\psi_{n,\ell,m}(\mathrm{I}) \equiv R_{n,\ell}(\vec{r}_1)\,Y^{m}_{\ell}(\theta_1,\phi_1) \equiv \left|R_{n,\ell}(\mathrm{I})\right\rangle \left|Y^{m}_{\ell}(\mathrm{I})\right\rangle \quad , \tag{21}$$

where the $R_{n,\ell}(\vec{r})$ and $Y^{m}_{\ell}(\theta,\phi)$ are also defined in Reference 7.

The specific eigenfunctions $\psi_{n,\ell,m}$ used in this calculation are those corresponding to the ground state for which $n = 1$, $\ell = 0$, $m = 0$;

$$\psi_{1,0,0} \equiv \left| R_{1,0} \right\rangle \left| Y_0^0 \right\rangle = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}} \quad , \tag{22}$$

and for the 2p states for which $n = 2$, $\ell = 1$, $m = 0, \pm 1$:

$$\psi_{2,1,0} \equiv \left| R_{2,1} \right\rangle \left| Y_1^0 \right\rangle = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}} \cos\theta \quad , \tag{23}$$

$$\psi_{2,1,+1} \equiv \left| R_{2,1} \right\rangle \left| Y_1^{+1} \right\rangle = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}} \sin\theta \cos\phi , \tag{24}$$

$$\psi_{2,1,-1} \equiv \left| R_{2,1} \right\rangle \left| Y_1^{-1} \right\rangle = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}} \sin\theta \sin\phi \quad . \tag{25}$$

The above functions, together with the photon states, redefined as

$$\psi_{(N)}^{(0)}(r) \equiv \left| , \ldots N_\lambda(\vec{\kappa}), \ldots \right\rangle \quad , \tag{26}$$

and whose vacuum state is given by

$$\psi_{(0)}^{(0)}(r) \equiv \left| , \ldots 0, \ldots \right\rangle \quad , \tag{27}$$

completely define the system under consideration.

System Eigenvalues

Having defined the eigenfunctions and their various forms, one proceeds to describe the eigenvalues corresponding to the above eigenfunctions. First, the hydrogenic eigenfunctions are solutions for the unperturbed state of the system. The photon states are eigenstates of the radiation field Hamiltonian H_r given by equation (4); that is,

$$\sum_{\kappa}\sum_{\lambda} \hbar c \kappa\, \mathcal{A}^{+}_{\lambda}(\vec{\kappa})\, \mathcal{A}_{\lambda}(\vec{\kappa}) \Big|, \ldots N_{\lambda}(\vec{\kappa}), \ldots \Big\rangle$$

$$= \sum_{\kappa}\sum_{\lambda} \hbar c \kappa\, N_{\lambda}(\vec{\kappa}) \Big|, \ldots N_{\lambda}(\vec{\kappa}), \ldots \Big\rangle \quad . \tag{28}$$

In addition, these photon states satisfy the usual relations given below:

$$\mathcal{A}^{+} \Big|, \ldots N, \ldots \Big\rangle = \sqrt{(N+1)} \Big|, \ldots (N+1), \ldots \Big\rangle \quad , \tag{29}$$

$$\mathcal{A} \Big|, \ldots N, \ldots \Big\rangle = \sqrt{(N)} \Big|, \ldots (N-1), \ldots \Big\rangle \quad , \tag{30}$$

$$\mathcal{A}^{+}\mathcal{A} \Big|, \ldots N, \ldots \Big\rangle = \sqrt{(N)}\,\sqrt{(N)} \Big|, \ldots N, \ldots \Big\rangle \quad , \tag{31}$$

$$\mathcal{A}\,\mathcal{A}^{+} \Big|, \ldots N, \ldots \Big\rangle = \sqrt{(N+1)}\,\sqrt{(N+1)} \Big|, \ldots N, \ldots \Big\rangle \quad . \tag{32}$$

It is clear from equation (28) that the vacuum state is an eigenstate of H_r with eigenvalue $N = 0$; hence, one is justified in including H_r with the unperturbed portion of the Hamiltonian.

Other relations between the photon eigenstates and the field operators which will be used later on are given below for future reference [8]:

$$\mathcal{A}^{+}_{\lambda}(\vec{\kappa})\, \mathcal{A}_{\lambda'}(\vec{\kappa'}) \Big|, N_{\lambda}(\vec{\kappa}), \ldots N'_{\lambda'}(\vec{\kappa'}), \Big\rangle$$

$$= \sqrt{N'}\,\sqrt{(N+1)} \Big|(N+1)_{\lambda}(\vec{\kappa}), \ldots (N-1)'_{\lambda'}(\vec{\kappa'}) \Big\rangle \quad , \tag{33}$$

$$
\mathcal{A}_{\lambda}(\vec{\kappa})\, \mathcal{A}^{+}_{\lambda'}(\vec{\kappa}') \Big| \, , \, N_{\lambda}(\vec{\kappa}), \, \ldots \, N'_{\lambda'}(\vec{\kappa}'), \Big\rangle
$$

$$
= \sqrt{(N+1)'}\, \sqrt{N} \, \Big| (N-1)_{\lambda}(\vec{\kappa}), \, \ldots \, (N+1)'_{\lambda'}(\vec{\kappa}') \Big\rangle \quad , \tag{34}
$$

$$
\mathcal{A}^{+}_{\lambda}(\vec{\kappa})\, \mathcal{A}^{+}_{\lambda'}(\vec{\kappa}') \Big| \, , \, N_{\lambda}(\vec{\kappa}), \, \ldots \, N'_{\lambda'}(\vec{\kappa}'), \Big\rangle
$$

$$
= \sqrt{(N+1)'}\, \sqrt{(N+1)} \, \Big| (N+1)_{\lambda}(\vec{\kappa}), \, \ldots \, (N+1)'_{\lambda'}(\vec{\kappa}') \Big\rangle \quad , \tag{35}
$$

$$
\mathcal{A}_{\lambda}(\vec{\kappa})\, \mathcal{A}_{\lambda'}(\vec{\kappa}') \Big| \, , \, N_{\lambda}(\vec{\kappa}), \, \ldots \, N'_{\lambda'}(\vec{\kappa}'), \Big\rangle
$$

$$
= \sqrt{N'}\, \sqrt{N} \, \Big| (N-1)_{\lambda}(\vec{\kappa}), \, \ldots \, (N-1)'_{\lambda'}(\kappa') \Big\rangle \quad . \tag{36}
$$

The energy eigenvalue for the system may now be expressed in terms of the unperturbed eigenfunctions using nondegenerate perturbation theory reported in an earlier NASA publication [9]. Thus, the solution to the perturbed eigenvalue problem,

$$
H\Psi_n = E_n \Psi_n \quad , \tag{37}
$$

may be obtained by expressing H as a series expansion of the form

$$
H = H^{(0)} + eH^{(1)} + e^2 H^{(2)} + e^3 H^{(4)} + e^4 H^{(4)} + \ldots \quad , \tag{38}
$$

whose eigenvalue may be expressed as

$$
E_n = E_n^{(0)} + e\, E_n^{(1)} + e^2 E_n^{(2)} + e^3 E_n^{(3)} + e^4 E_n^{(4)} + \ldots , \tag{39}
$$

where the energy corrections to ground state energy $E_n^{(0)}$ are given in terms of matrix elements of the perturbation Hamiltonians $H^{(i)}$, $i \neq 0$. Since one desires to obtain results to the fourth order, one needs all the terms indicated in equation (39). But since H as given by equation (38) contains only $H^{(1)}$ and $H^{(2)}$, one can obtain the terms corresponding to equation (39) directly from Reference 9, by letting $H^{(3)}$ and $H^{(4)}$ equal to zero. Doing this, the resulting expressions are:

$$E_n^{(1)} = H_{nn}^{(1)} \quad , \tag{40}$$

$$E_n^{(2)} = H_{nn}^{(2)} + \sum_{n'\neq n} \frac{H_{nn'}^{(1)} H_{n'n}^{(1)}}{\left(E_n^{(0)} - E_{n'}^{(0)}\right)} \quad , \tag{41}$$

$$\begin{aligned} E_n^{(3)} = & - H_{nn}^{(1)} \sum_{n'\neq n} \frac{H_{nn'}^{(1)} H_{n'n}^{(1)}}{\left(E_n^{(0)} - E_{n'}^{(0)}\right)^2} \\ & + \sum_{n'\neq n} \frac{\left(H_{nn'}^{(1)} H_{n'n}^{(2)} + H_{nn'}^{(2)} H_{n'n}^{(1)}\right)}{\left(E_n^{(0)} - E_{n'}^{(0)}\right)} \\ & + \sum_{n'\neq n} \sum_{n''\neq n} \frac{H_{nn'}^{(1)} H_{n'n''}^{(1)} H_{n''n}^{(1)}}{\left(E_n^{(0)} - E_{n'}^{(0)}\right)\left(E_n^{(0)} - E_{n''}^{(0)}\right)} \quad , \end{aligned} \tag{42}$$

$$
\begin{aligned}
E_n^{(4)} = & \sum_{n' \neq n} \frac{H_{nn'}^{(2)} H_{n'n}^{(2)}}{\left(E_n^{(0)} - E_{n'}^{(0)}\right)} - E_n^{(2)} \sum_{n' \neq n} \frac{H_{nn'}^{(1)} H_{n'n}^{(1)}}{\left(E_n^{(0)} - E_{n'}^{(0)}\right)^2} \\
& + \sum_{n' \neq n} \frac{H_{nn'}^{(1)} H_{n'n}^{(1)} \left[\left(H_{n'n'}^{(1)}\right)^2 + \left(H_{nn}^{(1)}\right)^2\right]}{\left(E_n^{(0)} - E_{n'}^{(0)}\right)^3} \\
& - H_{nn}^{(1)} \sum_{n' \neq n} \sum_{n'' \neq n} \frac{H_{nn'}^{(1)} H_{n'n''}^{(1)} H_{n''n}^{(1)} \left(2E_n^{(0)} - E_{n'}^{(0)} - E_{n''}^{(0)}\right)}{\left(E_n^{(0)} - E_{n'}^{(0)}\right)\left(E_n^{(0)} - E_{n''}^{(0)}\right)^2} \\
& + \sum_{n' \neq n} \sum_{n'' \neq n} \frac{\left(H_{nn'}^{(2)} H_{n'n''}^{(1)} H_{n''n}^{(1)} + H_{nn'}^{(1)} H_{n'n''}^{(2)} H_{n''n}^{(1)} + H_{nn'}^{(1)} H_{n'n''}^{(1)} H_{n''n}^{(2)}\right)}{\left(E_n^{(0)} - E_{n'}^{(0)}\right)\left(E_n^{(0)} - E_{n''}^{(0)}\right)} \\
& + \sum_{n' \neq n} \sum_{n'' \neq n} \sum_{n''' \neq n} \frac{H_{nn'}^{(1)} H_{n'n''}^{(1)} H_{n''n'''}^{(1)} H_{n'''n}^{(1)}}{\left(E_n^{(0)} - E_{n'}^{(0)}\right)\left(E_n^{(0)} - E_{n''}^{(0)}\right)\left(E_n^{(0)} - E_{n'''}^{(0)}\right)}
\end{aligned}
\tag{43}
$$

The interaction energy E_n, given in equation (39), may be evaluated to the desired fourth order using the above results.

CALCULATION OF GENERAL MATRIX ELEMENTS

Introduction

Analysis of the terms in equations (40) through (43) shows that the corrections to the interaction energy $E_n^{(0)}$ consist of various matrix elements of the form

$$
H_{nn}^{(i)}, \quad H_{nn'}^{(i)}, \quad H_{n'n''}^{(i)}, \quad H_{n''n'''}^{(i)}, \quad i = 1, 2 \quad .
$$

These terms need to be evaluated and then combined in order to obtain the interaction energy between the two atoms. The above operations are simplifed considerably if one neglects those terms which correspond to interactions between the radiation field and either one of the atoms [10]. Thus in subsequent discussions E_n will refer to only the interaction energy between atoms I and II, either through electrostatic interactions or through the radiation field. In the course of evaluating the various corrections to the interaction energy, an analysis is made on all the terms which make up the overall interaction energy to fourth order.

First-Order Corrections

One proceeds to evaluate the various matrix elements corresponding to the $E_n^{(i)}$ energy corrections. The first-order correction $E_n^{(i)}$ is given by

$$E_n^{(1)} = H_{nn}^{(1)} \equiv \left\langle \psi_n^{(0)} \middle| H^{(1)} \middle| \psi_n^{(0)} \right\rangle \quad . \tag{44}$$

Using the unperturbed eigenfunctions given by equation (16), the definition for $H^{(1)}$ given by equation (13), and since $H_{I,II}^{(1)}$ affect only atoms I and II, equation (44) simplifies to

$$\begin{aligned} E_\alpha^{(1)} &= \left\langle \psi_n^{(0)}(I)\, \psi_{(N)}^{(0)}(r) \middle| H_I^{(1)} \middle| \psi_n^{(0)}(I)\, \psi_{(N)}^{(0)}(r) \right\rangle \\ &+ \left\langle \psi_n^{(0)}(II)\, \psi_{(N)}^{(0)}(r) \middle| H_{II}^{(1)} \middle| \psi_n^{(0)}(II)\, \psi_{(N)}^{(0)}(r) \right\rangle \quad . \end{aligned} \tag{45}$$

Before evaluating equation (45), one simplifies the expression for $H_I^{(1)}$ as given in equation (8) be recalling that in obtaining $\vec{A}(\vec{\rho})$, the condition $\nabla \cdot \vec{A}(\vec{\rho}) = 0$ was used. (See References 10 and 11 for details.) Since $\left[\vec{A}, \vec{P}\right] = -i\hbar \nabla \cdot \vec{A}$, one notes that $\vec{A}$ and $\vec{P}$ commute and $H_I^{(1)}$ may now be expressed as

$$H_I^{(1)} = \left(-\frac{2}{2\mu c}\right)\left(\frac{c}{i}\sqrt{\frac{2\pi\hbar}{\text{Vol.}}}\right)\sum_{\kappa,\lambda}\left(\frac{1}{c\kappa}\right)^{1/2}$$

$$\times \left\{ \mathcal{A}_\lambda(\vec{\kappa})\, e^{i\vec{\kappa}\cdot\vec{\rho}_1} - \mathcal{A}_\lambda^+(\vec{\kappa})\, e^{-i\vec{\kappa}\cdot\vec{\rho}_1} \right\} \hat{\epsilon}_\lambda(\kappa) \cdot \vec{P}_I(\vec{r}_1) \quad . \tag{46}$$

The specific position dependence in the above expression for $H_I^{(1)}$ is included because the operators $\vec{P}$ and $\vec{A}$ refer to two different coordinate systems. Their relationship is best described by Figure 2 which also gives the following relations:

$$\vec{\rho}_1 = \vec{R}_I + \vec{r}_1 \quad , \quad \vec{\rho}_2 = \vec{R}_{II} + \vec{r}_2 \quad , \tag{47}$$

where $\vec{R}_I$ and $\vec{R}_{II}$ are related by (Fig. 1)

$$\vec{R} = \vec{R}_{II} - \vec{R}_I \quad . \tag{48}$$

Analysis of terms in equation (46) shows that $H_I^{(1)}$ consists of products proportional to

$$\mathcal{A}_\lambda(\vec{\kappa})\,\hat{\epsilon}_\lambda(\vec{\kappa}) \cdot \vec{P}_I(\vec{r}_1) \quad , \quad \mathcal{A}_\lambda^+(\vec{\kappa})\,\hat{\epsilon}_\lambda(\vec{\kappa}) \cdot \vec{P}_I(\vec{r}_1) \quad . \tag{49}$$

Since the momentum operators act only on the atomic states, and the field operators $\mathcal{A}_\lambda(\vec{\kappa})$, $\mathcal{A}_\lambda^+(\vec{\kappa})$ affect only photon states, one obtains

$$\mathcal{A}_\lambda(\vec{\kappa})\,\hat{\epsilon}_\lambda(\vec{\kappa}) \cdot \vec{P}_I(\vec{r}_1) \left| \psi_n^{(0)}(I)\, \psi_{(N)}^{(0)}(r) \right\rangle$$

$$= \hat{\epsilon}_\lambda(\vec{\kappa})\sqrt{N} \left| \psi_{(N-1)}^{(0)}(r) \right\rangle \cdot \vec{P}_I(\vec{r}_1) \left| \psi_n^{(0)}(I) \right\rangle \quad .$$

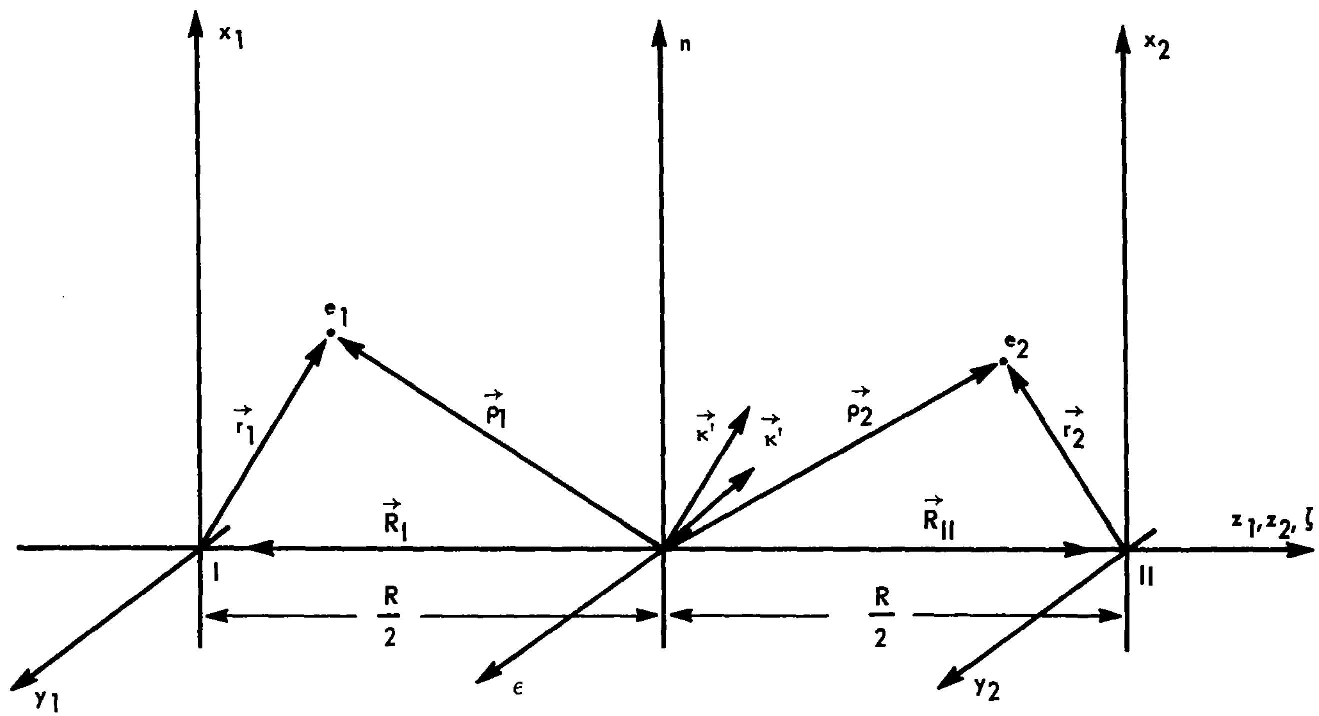


Figure 2. Electromagnetic potential coordinates.

Using this result, the first term in equation (45) is proportional to

$$\left\langle \psi^{(0)}_{(N)}(r) \middle| \psi^{(0)}_{(N-1)}(r) \right\rangle \left\langle \psi^{(0)}_{n}(I) \middle| \vec{P}_I(\vec{r}_1) \middle| \psi^{(0)}_{n}(I) \right\rangle \quad .$$

Terms of this type vanish, since one must satisfy the relations [8]

$$\left\langle , N', \ldots \middle| \mathfrak{a} \middle| N, \ldots \right\rangle = \sqrt{N}\ \delta_{N', (N-1)}$$

and

$$\left\langle , N', \ldots \middle| \mathfrak{a}^{+} \middle| N, \ldots \right\rangle = \sqrt{N+1}\ \delta_{N', (N+1)}$$

between initial and final photon states. Hence, the terms in equation (45) vanish and the first order correction $E^{(1)}_n$ does not contribute; that is,

$$E^{(1)}_n = H^{(1)}_{nn} = 0 \quad . \tag{50}$$

Second-Order Corrections

The second-order correction to the interaction energy is given by

$$E^{(2)}_{\alpha} = H^{(2)}_{\alpha\alpha} + \sum_{\alpha' \neq \alpha} \frac{H^{(1)}_{\alpha\alpha'} H^{(1)}_{\alpha'\alpha}}{\left(E^{(0)}_{\alpha} - E^{(0)}_{\alpha'}\right)} \quad . \tag{51}$$

Since $E^{(2)}_{\alpha}$ contains both $H^{(1)}$ and $H^{(2)}$, one first evaluates $H^{(2)}$ in terms of $\vec{A}(\vec{\rho})$. From equation (14), one notes that $H^{(2)}$ consists of $H^{(2)}_{I}$, $H^{(2)}_{II}$ and $H^{(2)}_{q}$. Since $H^{(2)}_{I}$ is given in terms of $\vec{A}(\vec{\rho})$, one uses equation (5) to get

$$H_I^{(2)} = \left(\frac{1}{2\mu c^2}\right)\left(\frac{2\pi\hbar c^2}{\text{Vol.}}\right) \sum_{\kappa\lambda} \sum_{\kappa'\lambda'} \left(\frac{1}{c^2 \kappa\kappa'}\right)^{1/2}$$

$$\times \Bigg\{ \mathcal{a}_\lambda(\vec{\kappa})\, \mathcal{a}^+_{\lambda'}(\vec{\kappa}')\, e^{i(\vec{\kappa} - \vec{\kappa}')\cdot\vec{\rho}_1} - \mathcal{a}_\lambda(\vec{\kappa})\, \mathcal{a}_{\lambda'}(\vec{\kappa}')\, e^{i(\vec{\kappa} + \vec{\kappa}')\cdot\vec{\rho}_1}$$

$$- \mathcal{a}^+_\lambda(\vec{\kappa})\, \mathcal{a}^+_\lambda(\vec{\kappa})\, e^{-i(\vec{\kappa} + \vec{\kappa}')\cdot\vec{\rho}_1}$$

$$+ \mathcal{a}^+_\lambda(\vec{\kappa})\, \mathcal{a}_{\lambda'}(\vec{\kappa}')\, e^{-i(\vec{\kappa} - \vec{\kappa}')\cdot\vec{\rho}_1} \Bigg\}\, \hat{\epsilon}_\lambda(\vec{\kappa}) \cdot \hat{\epsilon}_{\lambda'}(\vec{\kappa}') \quad . \tag{52}$$

Using the above definition for $H_I^{(2)}$, and the definition for $H^{(2)}$ given in equation (14), the first term in equation (51) becomes

$$H^{(2)}_{\alpha\alpha} = \left\langle I \,\middle|\, \frac{1}{2\mu c^2}\, \vec{A}_I(\vec{\rho}_1) \cdot \vec{A}_I(\vec{\rho}_1) \,\middle|\, I \right\rangle$$

$$+ \left\langle II \,\middle|\, \frac{1}{2\mu c^2}\, \vec{A}_{II}(\vec{\rho}_2) \cdot \vec{A}_{II}(\vec{\rho}_2) \,\middle|\, II \right\rangle$$

$$+ \left\langle I, II \,\middle|\, H_q^{(2)} \,\middle|\, I, II \right\rangle \quad . \tag{53}$$

Evaluation of the above terms is simplified by noting that the first two terms give the same result so that only two terms need to be evaluated. Rewriting the first term, one obtains

$$\left\langle \psi_n^{(0)}(I)\, \psi^{(0)}_{(N)}(r) \,\middle|\, \left(\frac{1}{2\mu c^2}\right) \vec{A}(\vec{\rho}_1) \cdot \vec{A}(\vec{\rho}_1) \,\middle|\, \psi_n^{(0)}(I)\, \psi_{(N)}(r) \right\rangle \quad . \tag{54}$$

Since the operator $\vec{A} \cdot \vec{A}$ consists of products of the form $\mathcal{a}^+\mathcal{a}$, $\mathcal{a}^+\mathcal{a}^+$, $\mathcal{a}\mathcal{a}^+$, $\mathcal{a}\mathcal{a}$, the above expression may be solved by applying the relations listed in equations (29) through (36). These relations indicate that only the term containing $\mathcal{a}\mathcal{a}^+$ gives results which are nonzero; that is,

$$\left\langle N_\lambda(\vec{\kappa}) \middle| \mathfrak{a}_\lambda(\vec{\kappa})\, \mathfrak{a}^+_{\lambda'}(\vec{\kappa}') \middle| N_\lambda(\vec{\kappa}) \right\rangle = \left\{ (N+1)_\lambda(\vec{\kappa}) \right\} \delta_{\lambda\lambda'}\, \delta_{\kappa\kappa'} \quad . \quad (55)$$

Using this expression in the matrix element, expression (54) yields

$$\left\langle \psi_n^{(0)}(I) \middle| \left(\frac{2\pi\hbar c^2}{2\mu c^2\,\mathrm{Vol.}}\right) \sum_{\kappa\lambda} \sum_{\kappa'\lambda'} \left(\frac{1}{c^2\kappa\kappa'}\right)^{1/2} \left\{ (N+1)_\lambda(\vec{\kappa}) \right\} \delta_{\lambda,\lambda'}\, \delta_{\kappa,\kappa'}\, e^{i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{\rho}_1}\, \hat{\epsilon}_\lambda(\vec{\kappa}) \cdot \hat{\epsilon}_{\lambda'}(\vec{\kappa}') \middle| \psi_n^{(0)}(I) \right\rangle .$$

Separating the sums over κ, λ and κ', λ', and summing over λ, λ' and κ', gives

$$\left\langle \psi_n^{(0)}(I) \middle| \left(\frac{2\pi\hbar c^2}{2\mu c^2\,\mathrm{Vol.}}\right) \sum_\kappa \left(\frac{2}{c\kappa}\right) (N+1)\,(\kappa) \middle| \psi_n^{(0)}(I) \right\rangle . \quad (56)$$

The above term is significant because it shows explicitly how the R dependence contained within the exponential $e^{i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{\rho}_1}$ vanishes when calculations are carried out to the second order, making the quantity in expression (56) independent of the interatomic separation. Terms having this property do not contribute to the interaction energy between atoms I and II and only give rise to self-interaction energies which are neglected in this calculation. Hence, the first two terms of equation (53) do not contribute. The last term of equation (53) is given by

$$\left\langle \psi_n^{(0)}(I)\, \psi_n^{(0)}(II) \middle| H_q^{(2)} \middle| \psi_n^{(0)}(I)\, \psi_n^{(0)}(II) \right\rangle \equiv \left\langle \alpha \middle| H_q^{(2)} \middle| \alpha \right\rangle . \quad (57)$$

This term corresponds to the electrostatic interaction between the two atoms and, as such, contributes to the interaction energy. Since all other terms vanish, equation (53) is given by

$$H_{\alpha\alpha}^{(2)} = \left\langle \alpha \middle| H_q^{(2)} \middle| \alpha \right\rangle . \quad (58)$$

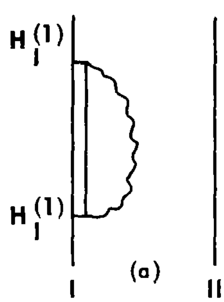
Expressing $H^{(1)}$ in terms of $H_I^{(1)}$ and $H_{II}^{(1)}$, the numerator of the second term in equation (53) becomes

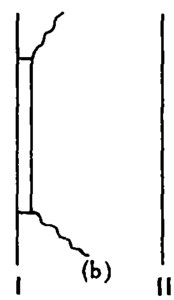
$$H^{(1)}_{\alpha\alpha'}\, H^{(1)}_{\alpha'\alpha} = \Big\{ \langle \alpha | H^{(1)}_{I} | \alpha' \rangle \langle \alpha' | H^{(1)}_{I} | \alpha \rangle + \langle \alpha | H^{(1)}_{I} | \alpha' \rangle \langle \alpha' | H^{(1)}_{II} | \alpha \rangle$$
$$+ \langle \alpha | H^{(1)}_{II} | \alpha' \rangle \langle \alpha' | H^{(1)}_{I} | \alpha \rangle + \langle \alpha | H^{(1)}_{II} | \alpha' \rangle \langle \alpha' | H^{(1)}_{II} | \alpha \rangle \Big\} \,, \qquad (59)$$

where α' denotes all the quantum numbers for the intermediate states. Expanding the first term in equation (59) yields

$$\langle \alpha | H^{(1)}_{I} | \alpha' \rangle \langle \alpha' | H^{(1)}_{I} | \alpha \rangle = \Big\{ \langle \psi^{(0)}_{n}(I)\, \psi^{(0)}_{(N)}(r) | H^{(1)}_{I} | \psi^{(0)}_{n'}(I)\, \psi^{(0)}_{(N')}(r) \rangle \qquad (60)$$
$$\times \langle \psi^{(0)}_{n'}(I)\, \psi^{(0)}_{(N')}(r) | H^{(1)}_{I} | \psi^{(0)}_{n}(I)\, \psi^{(0)}_{(N)}(r) \rangle \Big\}\, \delta_{n, n''}(II) \quad .$$

Referring to the expression for $H^{(1)}_{I}$, one notes that it consists of two terms involving $\mathfrak{a}_{\lambda}(\vec{\kappa})$ and $\mathfrak{a}^{+}_{\lambda}(\vec{\kappa})$, which, when operating on the photon eigenstates, as previously stated, require that the initial and intermediate photon states differ by one photon. Since $\langle H^{(1)}_{I} \rangle \langle H^{(1)}_{I} \rangle$ is independent of the coordinates of atom II, a photon must be exchanged between the field and atom I to obtain nonzero results. This is illustrated below, using the following interaction diagrams [10].



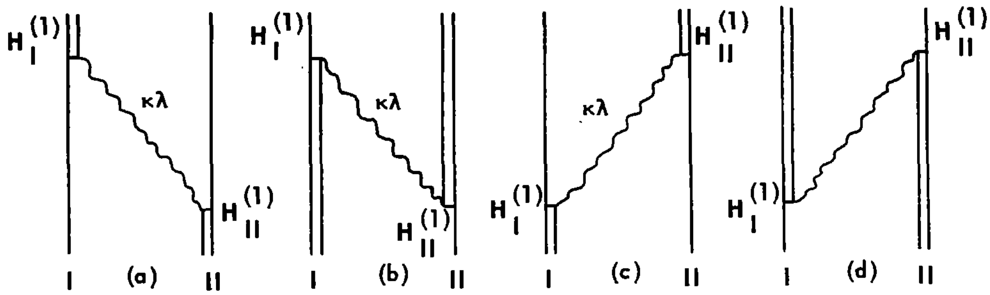


According to diagram (a), atoms I and II are initially in the same state (single lines), and the photon state corresponds to the vacuum state. The interaction operator $H^{(1)}_{I}$ "carries" the system into an intermediate state $|\alpha'\rangle$, where atom I is found in a different virtual (double line) state, atom II remains in its initial state, and the photon state contains one virtual photon [10]. The next interaction operator $H^{(1)}_{I}$ "brings" the system back to its original state. Diagram (b) illustrates the case in which the initial photon state is not the vacuum. If the initial system is such that both atoms are in the same state and the photon state corresponds to the vacuum, then only diagram (a) applies. Similar analysis on the fourth term of equation (59) yields identical results.

The second and third terms of equation (59) give similar results, as may be seen by considering the second term in its expanded form; that is,

$$\left\langle \alpha \left| H_{I}^{(1)} \right| \alpha' \right\rangle \left\langle \alpha' \left| H_{II}^{(1)} \right| \alpha \right\rangle = \left\langle \psi_{n}^{(0)}(I)\, \psi_{(N)}^{(0)}(r) \left| H_{I}^{(1)} \right| \psi_{n'}^{(0)}(I)\, \psi_{(N')}^{(0)}(r) \right\rangle \delta_{n,n''}(II)$$
$$\times \left\langle \psi_{n''}^{(0)}(II)\, \psi_{(N')}^{(0)}(r) \left| H_{II}^{(1)} \right| \psi_{n}^{(0)}(II)\, \psi_{(N)}^{(0)}(r) \right\rangle \delta_{n'n}(I) \quad . \tag{61}$$

To have nonvanishing results in equation (61), the photon states must differ by one photon. Hence, there must be a photon exchanged between atoms I and II because both $H_I^{(1)}$ and $H_{II}^{(1)}$ appear in the above matrix product. The only possible nonzero interactions are illustrated below.



Diagrams (a) and (b) correspond to $\left\langle H_{I}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle$; (c) and (d) correspond to $\left\langle H_{II}^{(1)} \right\rangle \left\langle H_{I}^{(1)} \right\rangle$. Analysis of these diagrams shows that the conditions of equation (61) cannot be met since the atomic states change in the transition from initial to intermediate state during photon exchange. Hence, the second and third terms of equation (59) do not contribute either. Therefore, the second term of $E_\alpha^{(2)}$ is identically zero. Since the second term of $E_\alpha^{(2)}$ vanishes, only the term given by equation (58) contributes to the second-order correction; that is,

$$E_\alpha^{(2)} = \left\langle \alpha \left| H_q^{(2)} \right| \alpha \right\rangle \quad . \tag{62}$$

Later, it will be shown that this term vanishes when the unperturbed states are s-states.

Third-Order Corrections

The third-order correction $E_\alpha^{(3)}$ is given by equation (42). Since $H_{nn}^{(1)}$ has been shown to vanish, $E_\alpha^{(3)}$ is given by

$$
\begin{aligned}
E_\alpha^{(3)} &= \sum_{\alpha' \neq \alpha} \frac{\left(H_{\alpha\alpha'}^{(1)} H_{\alpha'\alpha}^{(2)} + H_{\alpha\alpha'}^{(2)} H_{\alpha'\alpha}^{(1)}\right)}{\left(E_\alpha^{(0)} - E_{\alpha'}^{(0)}\right)} \\
&+ \sum_{\alpha' \neq \alpha} \sum_{\alpha'' \neq \alpha} \frac{H_{\alpha\alpha'}^{(1)} H_{\alpha'\alpha''}^{(1)} H_{\alpha''\alpha}^{(1)}}{\left(E_\alpha^{(0)} - E_{\alpha'}^{(0)}\right)\left(E_\alpha^{(0)} - E_{\alpha''}^{(0)}\right)} \quad . \qquad (63)
\end{aligned}
$$

Considering the factors in the first term, one notes that only one of them needs to be examined in detail, since the other factor is similar in form. Using equations (13) and (14) and expanding $H_{\alpha\alpha'}^{(1)} H_{\alpha'\alpha}^{(2)}$, one obtains

$$
\begin{aligned}
\left\langle H_I^{(1)} \right\rangle \left\langle H_I^{(2)} \right\rangle = \Big\{ & \left\langle \psi_n^{(0)}(I)\, \psi_{(N)}^{(0)}(r) \middle| H_I^{(1)} \middle| \psi_{n'}^{(0)}(I)\, \psi_{(N')}^{(0)}(r) \right\rangle \\
& \times \left\langle \psi_{n'}^{(0)}(I)\, \psi_{(N')}^{(0)}(r) \middle| H_I^{(2)} \middle| \psi_n^{(0)}(I)\, \psi_{(N)}^{(0)}(r) \right\rangle \Big\} \delta_{n,n''}(II) \qquad (64)
\end{aligned}
$$

Further expansion of the first term of equation (64) gives

$$
\begin{aligned}
H_{\alpha\alpha'}^{(1)} H_{\alpha'\alpha}^{(2)} = & \left\langle \alpha \middle| H_I^{(1)} \middle| \alpha' \right\rangle \left\langle \alpha' \middle| H_I^{(2)} \middle| \alpha \right\rangle + \left\langle \alpha \middle| H_I^{(1)} \middle| \alpha' \right\rangle \left\langle \alpha' \middle| H_{II}^{(2)} \middle| \alpha \right\rangle \\
& + \left\langle \alpha \middle| H_I^{(1)} \middle| \alpha' \right\rangle \left\langle \alpha' \middle| H_q^{(2)} \middle| \alpha' \right\rangle + \left\langle \alpha'' \middle| H_{II}^{(1)} \middle| \alpha \right\rangle \left\langle \alpha \middle| H_I^{(2)} \middle| \alpha' \right\rangle \\
& + \left\langle \alpha \middle| H_{II}^{(1)} \middle| \alpha' \right\rangle \left\langle \alpha \middle| H_{II}^{(2)} \middle| \alpha'' \right\rangle + \left\langle \alpha'' \middle| H_{II}^{(1)} \middle| \alpha \right\rangle \left\langle \alpha \middle| H_q^{(2)} \middle| \alpha' \right\rangle
\end{aligned}
$$

The condition $\delta_{n,n''}(II)$ requires that atom II remain in its initial state during the interaction between atom I and the electromagnetic field. In addition, the operator $H_I^{(1)}$ couples only photon states whose number of photons differs by unity, and $H_I^{(2)}$ couples photon states whose number of photons differs by zero or two. Therefore, the only way to satisfy both requirements is to allow the initial state $\left| \psi_{(N)}^{(0)}(r) \right\rangle$ to contain one photon. This is not allowed since $\left| \psi_{(N)}^{(0)}(r) \right\rangle$ must be the vacuum state; consequently, the above term cannot contribute to the interaction energy.

Referring to equation (64), one notes that the preceding discussion also applies to the fifth term by simply interchanging atoms. Similar arguments are used to show that the second and fourth terms of equation (64) do not contribute either. Finally, the third and sixth terms of equation (64), which contain matrix products of the operators $H_q^{(2)}$ and $H_{I,II}^{(1)}$, do not contribute because, as noted before, $H_{I,II}^{(1)}$ couple states whose number of photons differ by unity, and $H_q^{(2)}$ can only couple identical photon states. Applying the same arguments to $H_{\alpha\alpha'}^{(2)}$, $H_{\alpha'\alpha}^{(1)}$, one finds that the first term in equation (63) does not contribute to $E_\alpha^{(3)}$. Possible nonzero configurations corresponding to equation (64) are illustrated in Figure 3. These diagrams are introduced here only to illustrate the method used to analyze more complex situations later on.

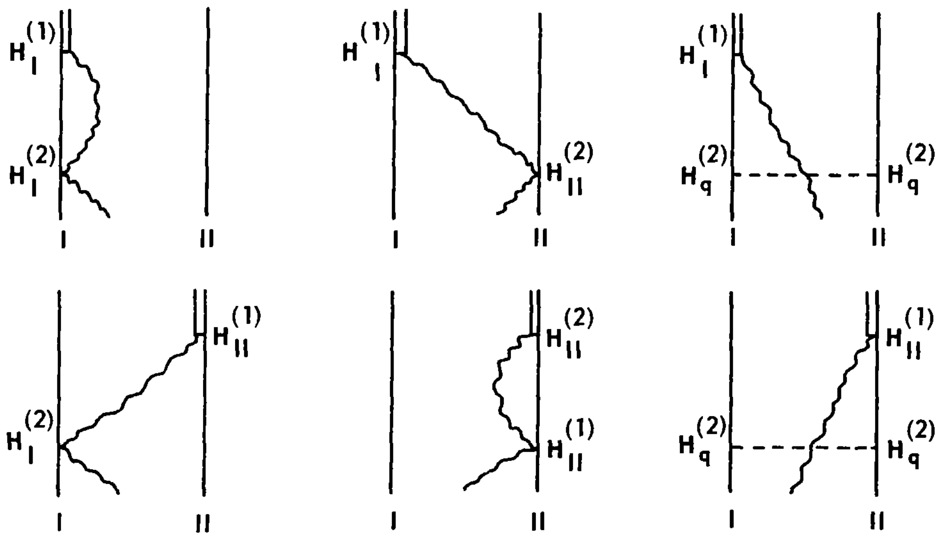


Figure 3. Possible nonzero interaction diagrams of equation (64).

The last term of equation (63) consists of matrix products involving $H^{(1)}$ only. Using equation (13) to expand this term, one obtains

$$\left\{ H^{(1)}_{\alpha\alpha'}\, H^{(1)}_{\alpha'\alpha''}\, H^{(1)}_{\alpha''\alpha} \right\}$$

$$= \left\langle \alpha \middle| H_{I}^{(1)} \middle| \alpha' \right\rangle \left\langle \alpha' \middle| H_{I}^{(1)} \middle| \alpha'' \right\rangle \left\langle \alpha'' \middle| H_{I}^{(1)} \middle| \alpha \right\rangle$$

$$+ \left\langle \alpha \middle| H_{I}^{(1)} \middle| \alpha' \right\rangle \left\langle \alpha' \middle| H_{II}^{(1)} \middle| \alpha'' \right\rangle \left\langle \alpha'' \middle| H_{I}^{(1)} \middle| \alpha \right\rangle$$

$$+ \left\langle H_{I}^{(1)} \right\rangle \left\langle H_{I}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle + \left\langle H_{I}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle$$

$$+ \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{I}^{(1)} \right\rangle \left\langle H_{I}^{(1)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{I}^{(1)} \right\rangle$$

$$+ \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{I}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \quad . \tag{65}$$

In the above equation, three types of products involving $H_{I}^{(1)}$ and $H_{II}^{(1)}$ are found, products involving only $H_{I}^{(1)}$ or $H_{II}^{(1)}$ and products coupling $H_{I}^{(1)}$ and $H_{II}^{(1)}$ in various ways. If one requires that initial and final states be identical, one notes that all the above terms violate this requirement in one way or another. This can best be seen by analyzing the diagrams in Figure 4, which depict typical nonzero configurations of the terms in equation (65).

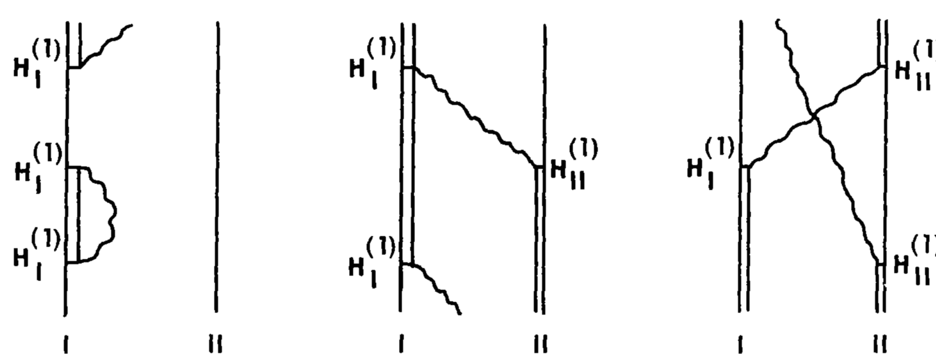


Figure 4. Some interaction diagrams of equation (65).

Since the last term is zero and the previous terms of equation (63) do not contribute either, one finds that the third-order correction to the interaction energy vanishes; that is,

$$E_n^{(3)} = 0 \qquad . \tag{66}$$

Fourth-Order Corrections

The fourth-order correction to the interaction energy is given by equation (43). Using the fact that $H_{nn}^{(1)}$ as well as the products of the form given by equation (59) vanish, the expression in equation (43) becomes

$$\begin{aligned}
\left\{ H_{\alpha\alpha'}^{(2)}, H_{\alpha'\alpha}^{(2)} \right\} = {} & \left\langle \alpha \left| H_I^{(2)} \right| \alpha' \right\rangle \left\langle \alpha' \left| H_I^{(2)} \right| \alpha \right\rangle \\
& + \left\langle \alpha \left| H_I^{(2)} \right| \alpha' \right\rangle \left\langle \alpha' \left| H_{II}^{(2)} \right| \alpha \right\rangle + \left\langle \alpha \left| H_I^{(2)} \right| \alpha' \right\rangle \left\langle \alpha' \left| H_q^{(2)} \right| \alpha \right\rangle \\
& + \left\langle H_{II}^{(2)} \right\rangle \left\langle H_I^{(2)} \right\rangle + \left\langle H_{II}^{(2)} \right\rangle \left\langle H_{II}^{(2)} \right\rangle + \left\langle H_{II}^{(2)} \right\rangle \left\langle H_q^{(2)} \right\rangle \\
& + \left\langle H_q^{(2)} \right\rangle \left\langle H_I^{(2)} \right\rangle + \left\langle H_q^{(2)} \right\rangle \left\langle H_{II}^{(2)} \right\rangle + \left\langle H_q^{(2)} \right\rangle \left\langle H_q^{(2)} \right\rangle
\end{aligned} \tag{67}$$

Expanding the first term of the above equation yields

$$\begin{aligned}
E_\alpha^{(4)} = {} & \sum_{\alpha'\neq\alpha} \frac{H_{\alpha\alpha'}^{(2)} H_{\alpha'\alpha}^{(2)}}{\left(E_\alpha^{(0)} - E_{\alpha'}^{(0)}\right)} \\
& + \sum_{\alpha'\neq\alpha} \sum_{\alpha''\neq\alpha} \frac{H_{\alpha\alpha'}^{(2)} H_{\alpha'\alpha''}^{(1)} H_{\alpha''\alpha}^{(1)} + H_{\alpha\alpha'}^{(1)} H_{\alpha'\alpha''}^{(2)} H_{\alpha''\alpha}^{(1)} + H_{\alpha\alpha'}^{(1)} H_{\alpha'\alpha''}^{(1)} H_{\alpha''\alpha}^{(2)}}{\left(E_\alpha^{(0)} - E_{\alpha'}^{(0)}\right)\left(E_\alpha^{(0)} - E_{\alpha''}^{(0)}\right)} \\
& + \sum_{\alpha'\neq\alpha} \sum_{\alpha''\neq\alpha} \sum_{\alpha'''\neq\alpha} \frac{H_{\alpha\alpha'}^{(1)} H_{\alpha'\alpha''}^{(1)} H_{\alpha''\alpha'''}^{(1)} H_{\alpha'''\alpha}^{(1)}}{\left(E_\alpha^{(0)} - E_{\alpha'}^{(0)}\right)\left(E_\alpha^{(0)} - E_{\alpha''}^{(0)}\right)\left(E_\alpha^{(0)} - E_{\alpha'''}^{(0)}\right)}
\end{aligned} \tag{68}$$

The three types of terms corresponding to various interactions in the above equation are analyzed as follows:

a. Interactions between field and either of the atoms: The first and fifth terms in equation (68) correspond to this type interaction. These terms do not contribute to the interaction energy as may be seen by analysis of diagrams (a) and (d) of Figure 5.

b. Interactions between field and both atoms: The second and fourth terms of equation (68) correspond to virtual photon exchange between atoms I and II and, as such, contribute to the interaction energy. [See diagrams (b) and (c) of Figure 5.] The terms in equation (68) involving both $H_q^{(2)}$ and $H_{I,II}^{(2)}$ are also in this category; except that the interaction between atoms takes place through the operator $H_q^{(2)}$, and the field interacts with either of the atoms via $H_{I,II}^{(2)}$. Hence, these terms contribute only when matrix elements over $H_q^{(2)}$ are nonzero. This group of terms is illustrated in Figure 6. Note that in this case $H_{I,II}^{(2)}$ gives rise to instantaneous emission and absorption or absorption and emission of two virtual photons. This requires that the initial and intermediate atomic states be the same. Therefore these terms contribute only when the matrix elements of $H_q^{(2)}$ over initial states are nonzero.

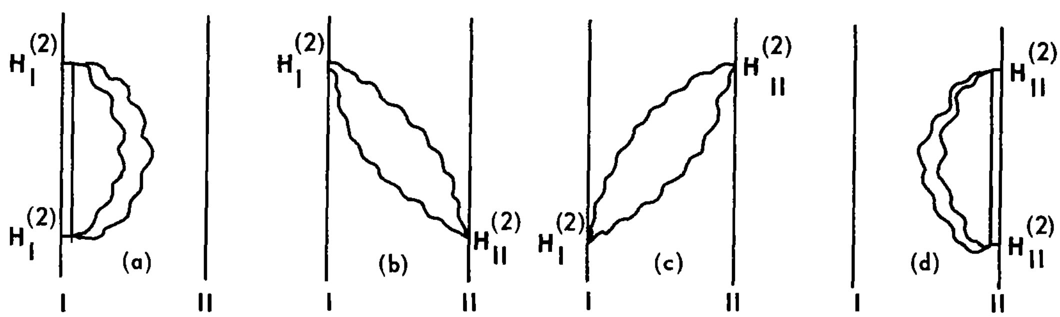


Figure 5. Interaction diagrams corresponding to first, second, fourth, and fifth terms of equation (68).

c. Interactions between atoms I and II only: The only term of this type is given by the last term in equation (68). Since $H_q^{(2)}$ does not affect the photon states, the initial, intermediate, and final photon states must be the

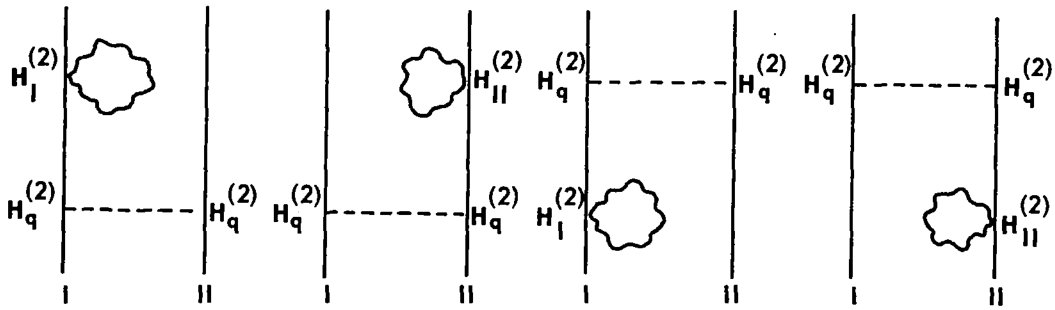


Figure 6. Interaction diagrams corresponding to the third, sixth, seventh, and eighth terms of equation (68).

same. The diagram corresponding to this term is given in Figure 7. Note that, when electromagnetic interactions are neglected, and the interaction energy is computed to fourth order in the electron charge $\underline{e}$, only this term and that given by equation (58) are obtained. This is the reason for singling out this term in Figure 7.

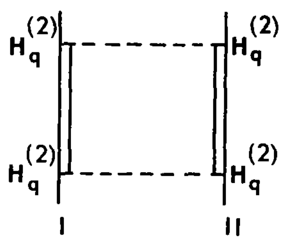


Figure 7. Interaction diagram corresponding to the atom-atom coulomb interaction term given by the last element of equation (68).

The second term of equation (67) is given by products of the form $H^{(2)}_{\alpha\alpha'} H^{(1)}_{\alpha'\alpha''} H^{(1)}_{\alpha''\alpha}$, $H^{(1)}_{\alpha\alpha'} H^{(2)}_{\alpha'\alpha''} H^{(1)}_{\alpha''\alpha}$, and $H^{(1)}_{\alpha\alpha'} H^{(1)}_{\alpha'\alpha''} H^{(2)}_{\alpha''\alpha}$. Using previous definitions for $H^{(1)}$ and $H^{(2)}$, the expansion of the above products is quite lengthy. These expansions are needed to select the nonzero terms which contribute to the interaction energy. If the indicated expansions are performed on only $H^{(2)}_{\alpha\alpha'} H^{(1)}_{\alpha'\alpha''} H^{(1)}_{\alpha''\alpha}$, and the results are expressed in terms of interaction diagrams, the task is simplified considerably. For the other two terms, only the resulting expansions and their corresponding interaction diagrams will be shown. To obtain the interaction diagrams, one uses previous results, illustrated in Figures 3, 4, 5, 6, and 7.

Expanding one of the terms yields the following:

$$
\begin{aligned}
&\left\{ H^{(2)}_{\alpha\alpha'} H^{(1)}_{\alpha'\alpha''} H^{(1)}_{\alpha''\alpha} \right\} \\
&= \left\langle \alpha \middle| H_I^{(2)} \middle| \alpha' \right\rangle \left\langle \alpha' \middle| H_I^{(1)} \middle| \alpha'' \right\rangle \left\langle \alpha'' \middle| H_I^{(1)} \middle| \alpha \right\rangle \\
&+ \left\langle \alpha \middle| H_I^{(2)} \middle| \alpha' \right\rangle \left\langle \alpha' \middle| H_I^{(1)} \middle| \alpha'' \right\rangle \left\langle \alpha'' \middle| H_{II}^{(1)} \middle| \alpha \right\rangle \\
&+ \left\langle H_I^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle + \left\langle H_I^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \\
&+ \left\langle H_{II}^{(2)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle + \left\langle H_{II}^{(2)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \\
&+ \left\langle H_{II}^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle + \left\langle H_{II}^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \\
&+ \left\langle H_q^{(2)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle + \left\langle H_q^{(2)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \\
&+ \left\langle H_q^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle + \left\langle H_q^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle .
\end{aligned}
\tag{69}
$$

In associating the above terms with an interaction diagram, one finds that some terms can have more than one possible configuration which gives nonzero results. This occurs especially for those nonzero terms which violate the requirement that final and initial states be the same. In other cases, one of the possible combinations corresponds to the term that contributes to the interaction energy. These situations are illustrated in Figure 8, where (a), (b), and (c) correspond to the first category, and (d), (e), and (f) to the latter cases.

Note that diagrams (a), (b), and (c) of Figure 8 do not contribute to the interaction energy and only (d) of the remaining group contributes. The photon states corresponding to diagrams (a), (b), and (c) in Figure 8 are:

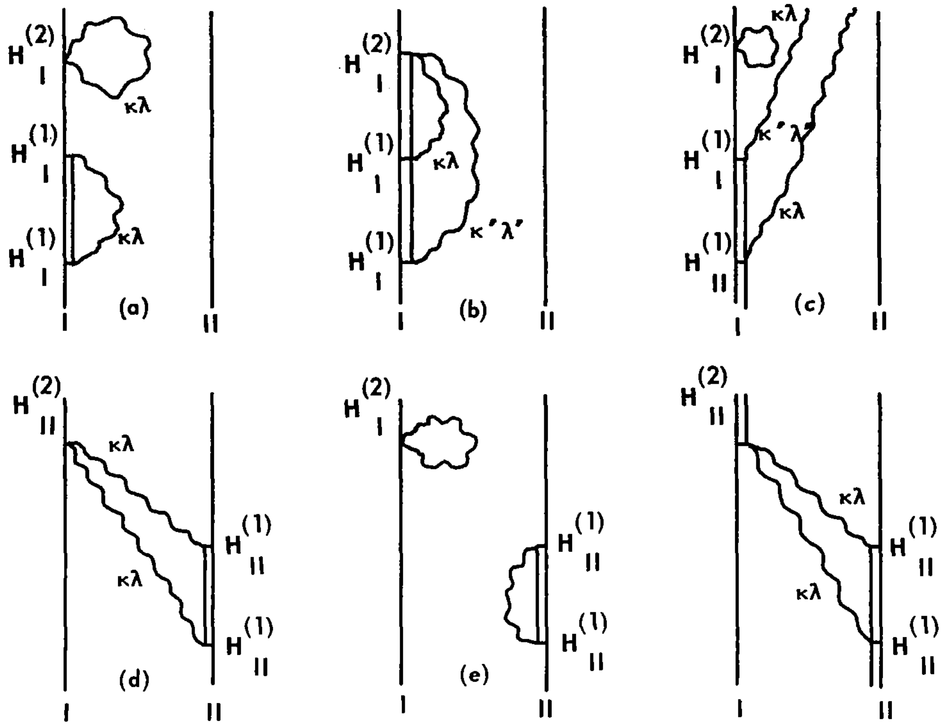


Figure 8. Interaction diagram corresponding to various nonzero configurations of terms in equation (69).

$$\text{(a)} \quad \langle 0 | \mathcal{A}_{\lambda}(\vec{\kappa})\, \mathcal{A}^{+}_{\lambda}(\vec{\kappa}) | 0 \rangle \langle 0 | \mathcal{A}_{\lambda}(\vec{\kappa}) | \kappa\lambda \rangle \langle \kappa\lambda | \mathcal{A}^{+}_{\lambda}(\vec{\kappa}) | 0 \rangle \quad ,$$

$$\text{(b)} \quad \langle 0 | \mathcal{A}_{\lambda}(\vec{\kappa})\, \mathcal{A}_{\lambda'}(\vec{\kappa}') | \kappa\lambda, \kappa'\lambda' \rangle \langle \kappa\lambda, \kappa'\lambda' | \mathcal{A}^{+}_{\lambda}(\vec{\kappa}) | \kappa'\lambda' \rangle \langle \kappa'\lambda' | \mathcal{A}^{+}_{\lambda'}(\vec{\kappa}') | 0 \rangle \quad ,$$

$$\text{(c)} \quad \langle \kappa\lambda, \kappa'\lambda' | \mathcal{A}_{\lambda}(\vec{\kappa})\, \mathcal{A}^{+}_{\lambda}(\vec{\kappa}) | \kappa\lambda, \kappa'\lambda' \rangle \langle \kappa\lambda, \kappa'\lambda' | \mathcal{A}^{+}_{\lambda'}(\vec{\kappa}') | \kappa\lambda \rangle \langle \kappa\lambda | \mathcal{A}^{+}_{\lambda}(\vec{\kappa}) | 0 \rangle \quad .$$

As one can see, these photon states may be associated with various intermediate states in the diagrams. The ordering of these states may be obtained by reading the matrix elements from right to left as one follows a diagram from the bottom up.

The interaction diagrams corresponding to the terms of equation (69) are listed in Figure 9; only one configuration for each term is shown, whether it contributes to the interaction energy or not. The listing of these diagrams is the same as the ordering of the terms in equation (69). Analysis of Figure 9 shows that only six diagrams contribute to the interaction energy: the fourth, fifth, and the last four. The remainder of the diagrams in Figure 9 correspond to either unacceptable situations or to self-interactions

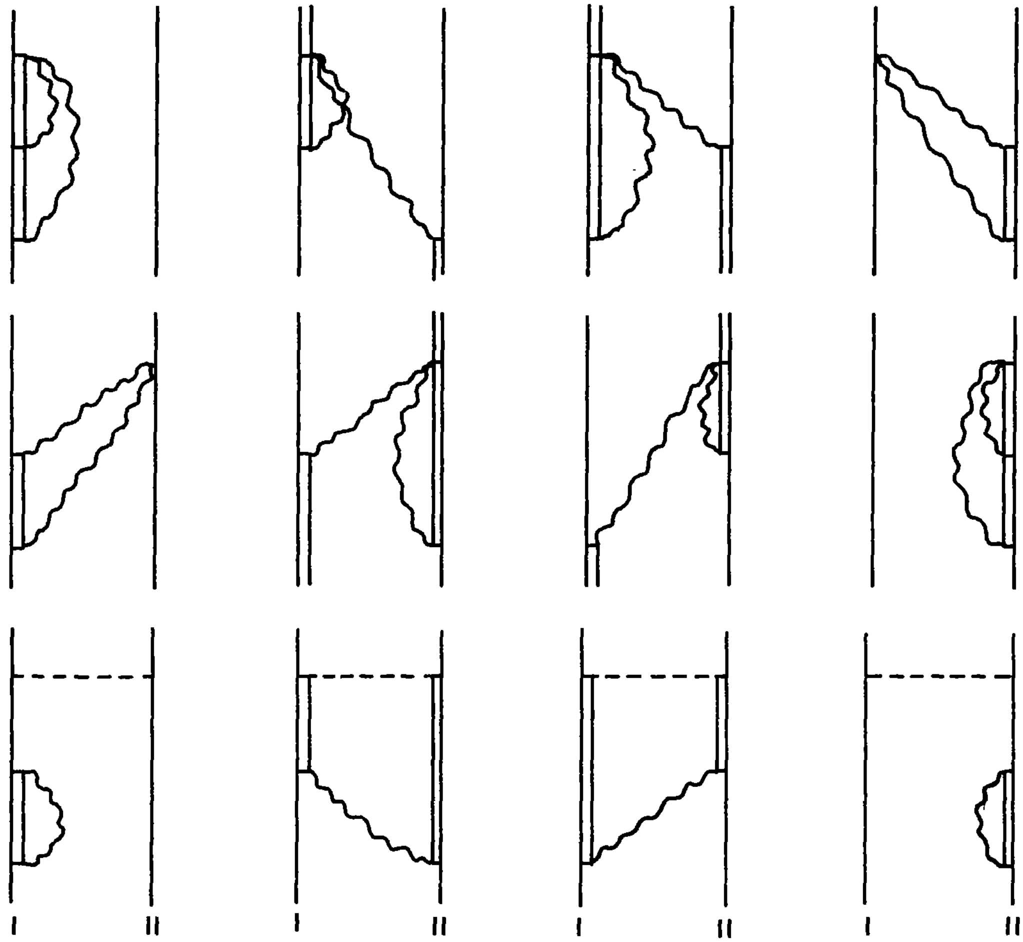


Figure 9. Interaction diagrams corresponding to terms of equation (69).

between either of the atoms and the radiation field. Of the six terms which contribute to the interaction energy, four involve the electrostatic interaction operator $H_q^{(2)}$ in two different ways. This can be seen by referring to the last four diagrams of Figure 9.

The next term to be considered, when expanded, gives

$$
\begin{aligned}
&\left\{ H^{(1)}_{\alpha\alpha'} \, H^{(1)}_{\alpha'\alpha''} \, H^{(1)}_{\alpha''\alpha} \right\} \\
&= \left\langle \alpha \middle| H_{I}^{(1)} \middle| \alpha' \right\rangle \left\langle \alpha' \middle| H_{I}^{(2)} \middle| \alpha'' \right\rangle \left\langle \alpha'' \middle| H_{I}^{(1)} \middle| \alpha \right\rangle \\
&+ \left\langle \alpha \middle| H_{I}^{(1)} \middle| \alpha' \right\rangle \left\langle \alpha' \middle| H_{I}^{(2)} \middle| \alpha'' \right\rangle \left\langle \alpha'' \middle| H_{II}^{(1)} \middle| \alpha \right\rangle \\
&+ \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{I}^{(2)} \right\rangle \left\langle H_{I}^{(1)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{I}^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \\
&+ \left\langle H_{I}^{(1)} \right\rangle \left\langle H_{II}^{(2)} \right\rangle \left\langle H_{I}^{(1)} \right\rangle + \left\langle H_{I}^{(1)} \right\rangle \left\langle H_{II}^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \\
&+ \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(2)} \right\rangle \left\langle H_{I}^{(1)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \\
&+ \left\langle H_{I}^{(1)} \right\rangle \left\langle H_{q}^{(2)} \right\rangle \left\langle H_{I}^{(1)} \right\rangle + \left\langle H_{I}^{(1)} \right\rangle \left\langle H_{q}^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \\
&+ \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{q}^{(2)} \right\rangle \left\langle H_{I}^{(1)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{q}^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \, . \qquad (70)
\end{aligned}
$$

The corresponding interaction diagrams are listed in Figure 10 where the rules outlined previously are applied to this case also.

Analysis of Figure 10 shows that six diagrams contribute to the interaction energy as before: the fourth, fifth, and the last four. The remainder are classified as in Figure 9.

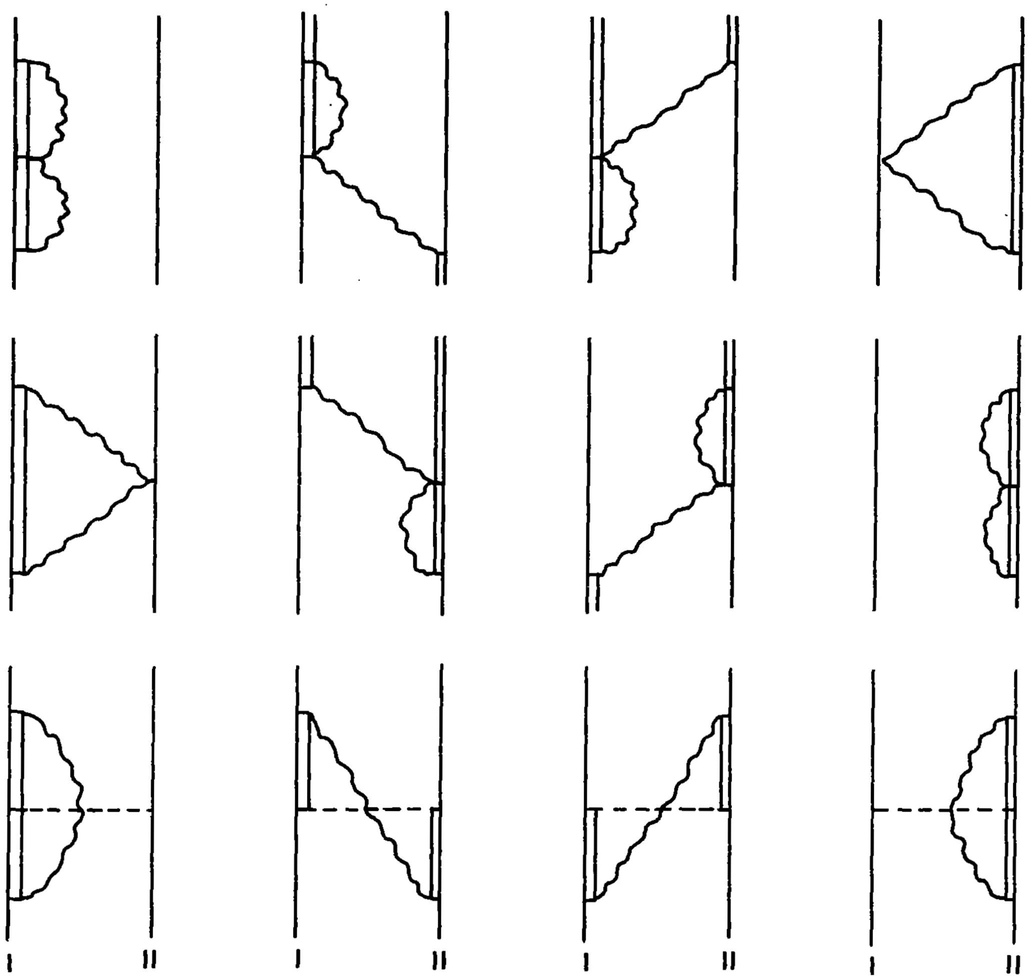


Figure 10. Interaction diagrams corresponding to terms in equation (70).

The last term in this group to be considered is given by

$$
\begin{aligned}
\left\{ H^{(1)}_{\alpha\alpha'}, H^{(1)}_{\alpha'\alpha''}, H^{(2)}_{\alpha''\alpha} \right\} &= \left\langle \alpha \middle| H_I^{(1)} \middle| \alpha' \right\rangle \left\langle \alpha' \middle| H_I^{(1)} \middle| \alpha'' \right\rangle \left\langle \alpha'' \middle| H_I^{(2)} \middle| \alpha \right\rangle \\
&+ \left\langle \alpha \middle| H_I^{(1)} \middle| \alpha' \right\rangle \left\langle \alpha' \middle| H_I^{(1)} \middle| \alpha'' \right\rangle \left\langle \alpha'' \middle| H_{II}^{(2)} \middle| \alpha \right\rangle \\
&+ \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(2)} \right\rangle + \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(2)} \right\rangle \\
&+ \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_I^{(2)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(2)} \right\rangle \\
&+ \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(2)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(2)} \right\rangle \\
&+ \left\langle H_I^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_q^{(2)} \right\rangle + \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_q^{(2)} \right\rangle \\
&+ \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_q^{(2)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_q^{(2)} \right\rangle
\end{aligned}
\tag{71}
$$

The corresponding set of interaction diagrams is given in Figure 11. Analysis of this figure shows that six more diagrams contribute to the interaction energy: the second, seventh, and the last four diagrams.

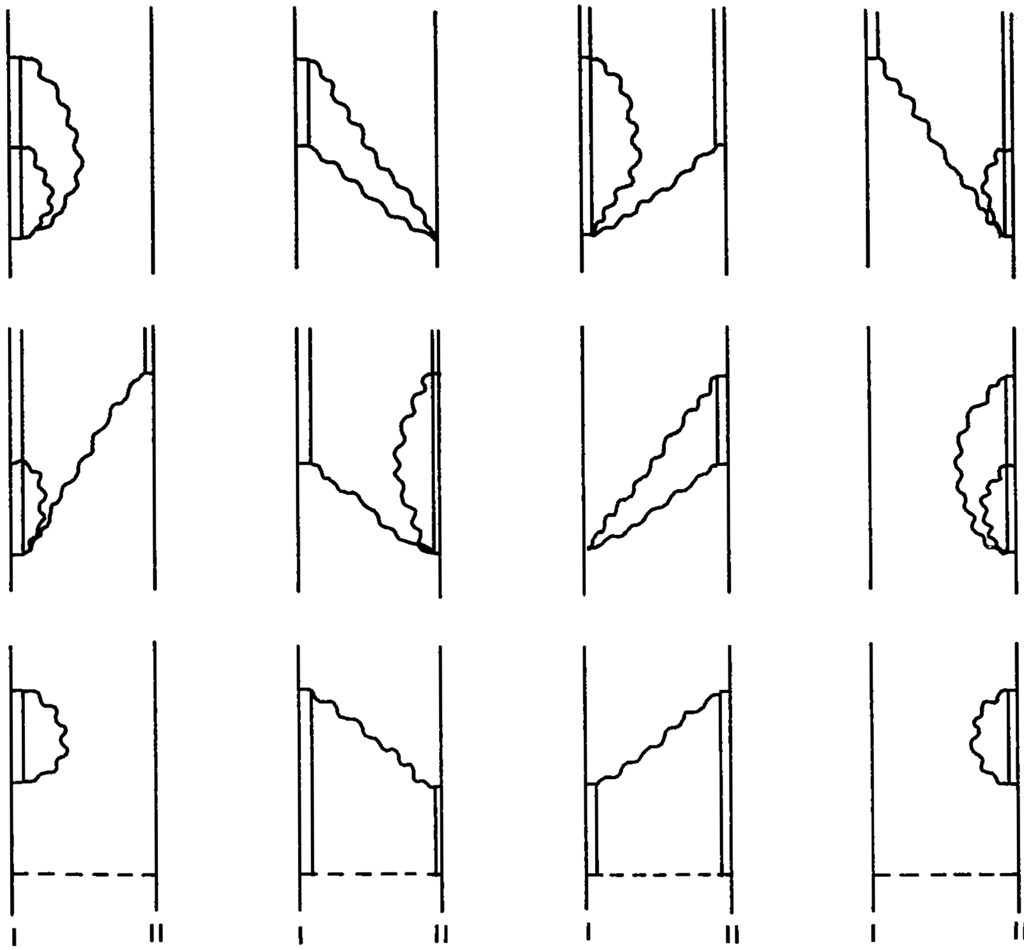


Figure 11. Interaction diagrams corresponding to terms in equation (71).

The importance of the preceding diagrams lies in the fact that one now finds nonzero terms which contain both the radiation field operators and the coulomb-type operator, $H_q^{(2)}$, coupled together within individual factors. The last four diagrams in Figures 9, 10, and 11, respectively, show the form of the interactions in a systematic and informative way. Later, it will be seen that these terms play a very important role in the evaluation of the interaction energy to various approximations. Instead of collecting the contributing terms just obtained, one evaluates the last term of equation (67) and then collects all the nonzero terms which contribute to the interaction energy.

Using the definitions for $H^{(1)}$, the last term in equation 67 expands into

$$
\begin{aligned}
&\left\{ H^{(1)}_{\alpha\alpha'} \, H^{(1)}_{\alpha'\alpha''} \, H^{(1)}_{\alpha''\alpha'''} \, H^{(1)}_{\alpha'''\alpha} \right\} \\
&= \langle \alpha | H_{I}^{(1)} | \alpha' \rangle \langle \alpha' | H_{I}^{(1)} | \alpha'' \rangle \langle \alpha'' | H_{I}^{(1)} | \alpha''' \rangle \langle \alpha''' | H_{I}^{(1)} | \alpha \rangle \\
&+ \langle \alpha | H_{I}^{(1)} | \alpha' \rangle \langle \alpha' | H_{I}^{(1)} | \alpha'' \rangle \langle \alpha'' | H_{I}^{(1)} | \alpha''' \rangle \langle \alpha''' | H_{II}^{(1)} | \alpha \rangle \\
&+ \langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle + \langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \\
&+ \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle + \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \\
&+ \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle + \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \\
&+ \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle + \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \\
&+ \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle + \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \\
&+ \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle + \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \\
&+ \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle + \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle
\end{aligned}
\tag{72}
$$

The terms in equation (72) contain various types of factors, corresponding to interactions between each individual atom and the electromagnetic field or between the electromagnetic field with both atoms. In order to illustrate those terms we again pick one representative interaction diagram for each of the terms which does not contribute to the interaction energy, but list the various combinations which do contribute. This is necessary since we have to consider all possible configurations as indicated by the sums over $\kappa, \lambda; \kappa', \lambda'$ of the operator $H_{I}^{(1)}$ in the various intermediate states. Until now, only one interaction diagram per term has been sufficient to take care of the nonzero terms. This is no longer sufficient when listing the possible configurations for this term. This point is illustrated by considering a specific term of equation (72) and listing the possible configurations of this term in Figure 12.

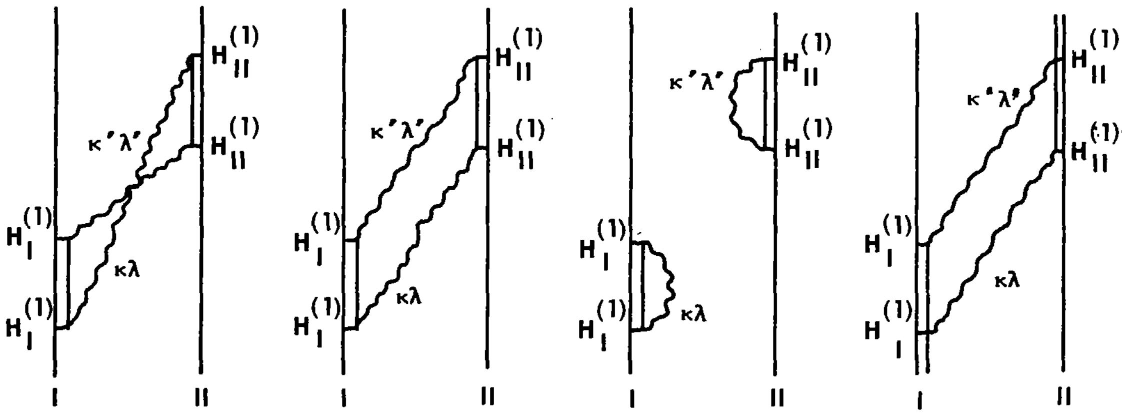


Figure 12. Interaction diagrams of some of the possible configurations corresponding to the 13th term of equation (72). (The photon parameters κ, λ; κ', λ' are included to show the variations in intermediate photon states.)

Analysis of Figure 12 shows that the first two diagrams are two possible nonzero configurations for the 13th term of equation (72), which contributes to the interaction energy.

The interaction diagrams corresponding to equation (72) are listed in Figure 13; one includes the various configurations for the terms which contribute to the interaction energy, and only a representative diagram is included for those terms which do not. When a given term contains both zero and nonzero configurations, the configurations which contribute are used. In Figure 13, the various interaction diagrams are numbered; those which correspond to the same term of equation (72) are denoted by primes [e.g., (4) and (4)' correspond to the fourth term of equation (72)]. Analysis of Figure 13 shows 12 diagrams corresponding to 6 different terms, in equation (72), which contribute to the interaction energy. This is by far the largest number of nonzero terms resulting from a single term in $E_\alpha^{(4)}$. One can see that out of a large number of possible combinations indicated by the sums over α', α'', α''', a number of terms do not contribute, solely because of the restrictions on the various photon states. Collecting all the terms which contribute to the interaction energy correction $E_\alpha^{(4)}$, one finally obtains

$$
\begin{aligned}
E_{\alpha}^{(4)} = \sum_{\alpha' \neq \alpha} \left(\frac{1}{E_{\alpha}^{(0)} - E_{\alpha'}^{(0)}} \right) \Big\{ & \langle H_{I}^{(2)} \rangle \langle H_{II}^{(2)} \rangle + \langle H_{II}^{(2)} \rangle \langle H_{I}^{(2)} \rangle \\
& + \langle H_{I}^{(2)} \rangle \langle H_{q}^{(2)} \rangle + \langle H_{II}^{(2)} \rangle \langle H_{q}^{(2)} \rangle \\
& + \langle H_{q}^{(2)} \rangle \langle H_{I}^{(2)} \rangle + \langle H_{q}^{(2)} \rangle \langle H_{II}^{(2)} \rangle + \langle H_{q}^{(2)} \rangle \langle H_{q}^{(2)} \rangle \Big\} \\
& + \sum_{\alpha' \neq \alpha} \sum_{\alpha'' \neq \alpha} \left[\frac{1}{\left(E_{\alpha}^{(0)} - E_{\alpha'}^{(0)}\right)\left(E_{\alpha}^{(0)} - E_{\alpha''}^{(0)}\right)} \right] \\
& \times \Big\{ \Big[\langle H_{I}^{(2)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle + \langle H_{II}^{(2)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \\
& \quad + \langle H_{q}^{(2)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle + \langle H_{q}^{(2)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \\
& \quad + \langle H_{q}^{(2)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle + \langle H_{q}^{(2)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \Big] \\
& \quad + \Big[\langle H_{II}^{(1)} \rangle \langle H_{I}^{(2)} \rangle \langle H_{II}^{(1)} \rangle + \langle H_{I}^{(1)} \rangle \langle H_{II}^{(2)} \rangle \langle H_{I}^{(1)} \rangle \\
& \quad + \langle H_{I}^{(1)} \rangle \langle H_{q}^{(2)} \rangle \langle H_{I}^{(1)} \rangle + \langle H_{I}^{(1)} \rangle \langle H_{q}^{(2)} \rangle \langle H_{II}^{(1)} \rangle \\
& \quad + \langle H_{II}^{(1)} \rangle \langle H_{q}^{(2)} \rangle \langle H_{I}^{(1)} \rangle + \langle H_{II}^{(1)} \rangle \langle H_{q}^{(2)} \rangle \langle H_{II}^{(1)} \rangle \Big] \\
& \quad + \Big[\langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(2)} \rangle + \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(2)} \rangle \\
& \quad + \langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{q}^{(2)} \rangle + \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{q}^{(2)} \rangle \\
& \quad + \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{q}^{(2)} \rangle + \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{q}^{(2)} \rangle \Big] \Big\} \\
& + \sum_{\alpha' \neq \alpha} \sum_{\alpha'' \neq \alpha} \sum_{\alpha''' \neq \alpha} \left[\frac{1}{\left(E_{\alpha}^{(0)} - E_{\alpha'}^{(0)}\right)\left(E_{\alpha}^{(0)} - E_{\alpha''}^{(0)}\right)\left(E_{\alpha}^{(0)} - E_{\alpha'''}^{(0)}\right)} \right] \\
& \times \Big[\langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \\
& + \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \\
& + \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \\
& + \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \\
& + \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \\
& + \langle H_{II}^{(1)} \rangle \langle H_{II}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \langle H_{I}^{(1)} \rangle \Big] \, .
\end{aligned} \tag{73}
$$

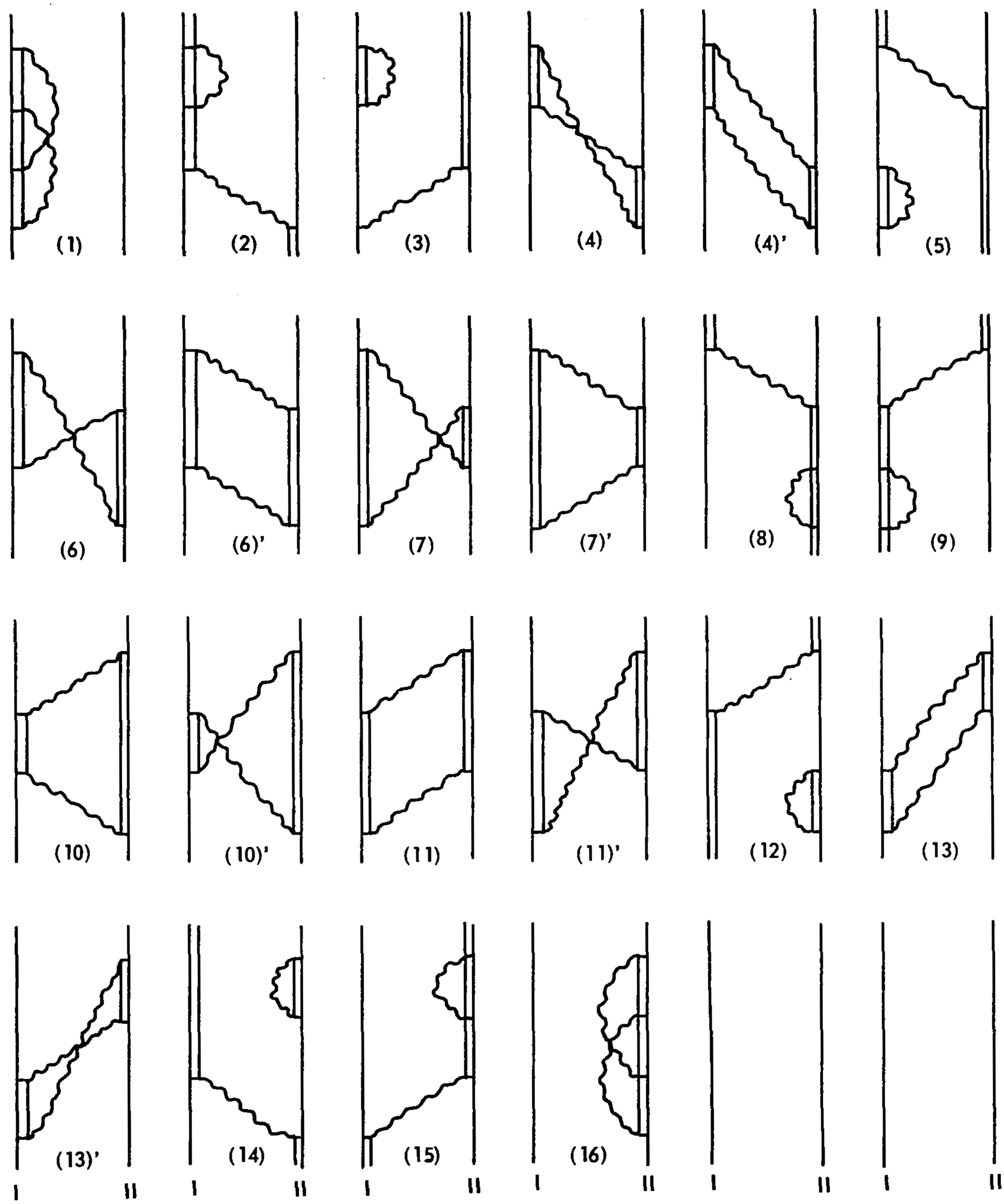


Figure 13. Interaction diagrams corresponding to equation (72).

Combining $E_\alpha^{(4)}$ with all the other nonzero corrections, one obtains the interaction energy E_α to the fourth order; that is,

$$E_\alpha = E_\alpha^{(0)} + e^2 E_\alpha^{(2)} + e^4 E_\alpha^{(4)} \quad , \tag{74}$$

where $E_\alpha^{(2)}$ and $E_\alpha^{(4)}$ are given by equations (62) and (73), respectively. It is easy to see why one must consider fourth-order corrections to the interaction energy when considering both electrostatic and electromagnetic interactions between atoms. In cases where $E_\alpha^{(2)}$ vanishes, the only contribution to the interaction energy comes from $E_\alpha^{(4)}$. In this case, $E_\alpha^{(4)}$ is simplified somewhat because several terms in equation (73) vanish.

INTERACTION ENERGY BETWEEN HYDROGENIC ATOMS IN THEIR GROUND STATE

Interaction Energy of the System

The unperturbed system in this case consists of atoms I and II initially in their ground state configuration (1s - 1s); the electromagnetic field is in its vacuum state $\left(\left|, \ldots 0, \ldots \right\rangle \right)$. From the previous discussion, the energy eigenvalue to the fourth order is given by

$$E_\alpha = E_\alpha^{(0)} + e^2 E_\alpha^{(2)} + e^4 E_\alpha^{(4)} \quad . \tag{75}$$

Since one is interested in the corrections to $E_\alpha^{(0)}$ rather than E_α, one rewrites equation (75) as

$$\Delta E_\alpha \equiv \left(E_\alpha - E_\alpha^{(0)} \right) = e^2 E_\alpha^{(2)} + e^{(4)} E_\alpha^{(4)} \quad , \tag{76}$$

where ΔE_α is defined as the correction to the ground state energy due to the interactions. Henceforth, this will be the only quantity of interest. To evaluate the terms in equation (76), one considers first $E_\alpha^{(2)}$, given by

$$E_\alpha^{(2)} = \left\langle \alpha \middle| H_q^{(2)} \middle| \alpha \right\rangle \quad . \tag{77}$$

In terms of equation (3), the above becomes

$$E_1^{(2)} = \left\langle I(1,0,0)\ II(1,0,0) \right| \left\langle ,0,\ \ldots \right| \sum_{L_1=1}^{\infty} \sum_{L_2=1}^{\infty} \frac{(-1)^{L_2} r_1^{L_1} r_2^{L_2} (4\pi)(L_1+L_2)!}{R^{L_1+L_2+1}\left[(2L_1+1)(2L_2+1)\right]^{1/2}}$$
$$\times \sum_{M=-L_<}^{M=+L_<} \frac{Y_{L_1}^{M*}(I)\, Y_{L_2}^{-M*}(II)}{\left[(L_1+M)!\,(L_1-M)!\,(L_2+M)!\,(L_2-M)!\right]^{1/2}} \left| I(1,0,0)\ II(1,0,0) \right\rangle \left| ,0,\ \ldots \right\rangle \tag{78}$$

Since the operator $H_q^{(2)}$ factors into quantities corresponding to atoms I and II and does not contain field operators, the above expression may be written as

$$E_1^{(2)} = \sum_{L_1}\sum_{L_2}\sum_{M} \frac{(-1)^{L_2}(4\pi)(L_1+L_2)!}{R^{L_1+L_2+1}\left[(2L_1+1)(2L_2+1)\right]^{1/2}\left[(L_1+M)!\,(L_1-M)!\,(L_2+M)!\,(L_2-M)!\right]^{1/2}}$$
$$\times \left\langle I(1,0,0) \middle| r_1^{L_1} Y_{L_1}^{M*}(\theta_1\phi_1) \middle| I(1,0,0) \right\rangle \left\langle II(1,0,0) \middle| r_2^{L_2} Y_{L_2}^{-M*}(\theta_2\phi_2) \middle| II(1,0,0) \right\rangle$$

Using the definition for the atomic eigenfunctions given in equation (18), the matrix elements in equation (79) factor into products of the form

$$\left\langle I(1,0,0) \middle| r_1^{L_1} Y_{L_1}^{M*} \middle| I(1,0,0) \right\rangle$$
$$= \left\langle R_{1,0}(I) \middle| r_1^{L_1} \middle| R_{1,0}(I) \right\rangle \left\langle Y_0^0(I) \middle| Y_{L_1}^{M*}(I) \middle| Y_0^0(I) \right\rangle \quad .$$

Using the relations between spherical harmonics [12],

$$\left\langle Y_{\ell_3}^{m_3} \middle| Y_{\ell_2}^{m_2 *} \middle| Y_{\ell_1}^{m_1} \right\rangle$$

$$= (-1)^{m_2} \left[\frac{(2\ell_1 + 1)(2\ell_2 + 1)}{4\pi\ (2\ell_3 + 1)} \right]^{1/2} C(\ell_1 \ell_2 \ell ; m_1, -m_2, m_3)\, C(\ell_1, \ell_2, \ell_3; 0, 0, 0), \tag{80}$$

one obtains

$$\left\langle Y_{\ell_1}^{m_1} \middle| Y_{L_1}^{M *} \middle| Y_{\ell_1}^{m_1} \right\rangle = \left(\frac{1}{4\pi} \right)^{1/2} \delta_{M,0}\, \delta_{L_1,0} \qquad ,$$

by setting $m_1 = m_3$ and $m_2 = M$. Substituting this, equation (79) reduces to

$$E_1^{(2)} = \sum_{L_1, L_2} \sum_{M} \frac{\delta_{M,0} (-1)^{L_2} (4\pi)(L_1 + L_2)! \left\langle R_{1,0}(I) \middle| r_1^{L_1} \middle| R_{1,0}(I) \right\rangle \left\langle R_{1,0}(II) \middle| r_2^{L_2} \middle| R_{1,0}(II) \right\rangle \delta_{L_1,0} \delta_{L_2,0}}{R^{L_1+L_2+1} \left[(2L_1 + 1)(2L_2 + 1)(L_1 - M)!(L_1 + M)!(L_2 - M)!(L_2 + M)! \right]^{1/2}} \quad . \tag{81}$$

Equation (81) shows that the only term in the series corresponds to the case where $L_1 = L_2 = 0$, and $M = 0$. This term is the monopole contribution of the electrostatic potential between the two atoms. When the charge distributions are neutral as is the case here, this term does not contribute. Hence, one sees that $E_1^{(2)}$ is identically zero for the case in which the atomic initial states are picked to be the (1s) ground states; that is

$$E_1^{(2)} = 0 \qquad . \tag{82}$$

With this result the second term in equation (76) is considerably simplified, since the various matrix elements involving the electrostatic operator $H_q^{(2)}$ will vanish when the atomic states considered correspond to the initial state. Identifying these factors in equation (73) and setting the terms containing them equal to zero, the expression for $E_1^{(4)}$ may be readily obtained. Since $E_1^{(2)}$ is zero, the resulting expression for $E_1^{(4)}$ is just $\Delta E/e^4$. Applying the above comments and rearranging terms in the expression for $E_1^{(4)}$, one obtains

$$
\begin{aligned}
\Delta E/e^4 = & \sum_{\alpha' \neq \alpha} \left(\frac{1}{E_\alpha^{(0)} - E_{\alpha'}^{(0)}} \right) \\
& \times \left\{ \left\langle H_q^{(2)} \right\rangle \left\langle H_q^{(2)} \right\rangle + \left\langle H_I^{(2)} \right\rangle \left\langle H_{II}^{(2)} \right\rangle + \left\langle H_{II}^{(2)} \right\rangle \left\langle H_I^{(1)} \right\rangle \right\} \\
& + \sum_{\alpha' \neq \alpha} \sum_{\alpha'' \neq \alpha} \left[\frac{1}{\left(E_\alpha^{(0)} - E_{\alpha'}^{(0)}\right)\left(E_\alpha^{(0)} - E_{\alpha''}^{(0)}\right)} \right] \\
& \times \left\{ \left\langle H_I^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle + \left\langle H_{II}^{(2)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \right. \\
& + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle + \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(2)} \right\rangle \left\langle H_I^{(1)} \right\rangle \\
& + \left\langle H_I^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(2)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(2)} \right\rangle \\
& + \left\langle H_q^{(2)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle + \left\langle H_q^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \\
& + \left\langle H_I^{(1)} \right\rangle \left\langle H_q^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_q^{(2)} \right\rangle \left\langle H_I^{(1)} \right\rangle \\
& \left. + \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_q^{(2)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_q^{(2)} \right\rangle \right\} \\
& + \sum_{\alpha' \neq \alpha} \sum_{\alpha'' \neq \alpha} \sum_{\alpha''' \neq \alpha} \left[\frac{1}{\left(E_\alpha^{(0)} - E_{\alpha'}^{(0)}\right)\left(E_\alpha^{(0)} - E_{\alpha''}^{(0)}\right)\left(E_\alpha^{(0)} - E_{\alpha'''}^{(0)}\right)} \right] \\
& \times \left\{ \left\langle H_I^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle + \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \right. \\
& + \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \\
& \left. + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle + \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_I^{(1)} \right\rangle \right\}
\end{aligned} \tag{83}
$$

The terms in equation (83) are then the nonzero quantities which need to be evaluated to get the interaction energy of the system to the fourth order in the electron charge $\underline{e}$. The interaction diagrams corresponding to these terms are summarized in Figure 14, in which all the possible nonzero combinations are included. Referring to Figure 14 one can see the reason for rearranging the terms in equation (73) before writing down equation (83). This rearrangement yields the following groupings:

a. The first diagram corresponds to the coulomb type interaction $\left\langle H_q^{(2)} \right\rangle \left\langle H_q^{(2)} \right\rangle$,

b. The next two correspond to interactions of the type $\left\langle H^{(2)} \right\rangle \left\langle H^{(2)} \right\rangle$,

c. The next six correspond to interactions of the type $\left\langle H^{(2)} \right\rangle \left\langle H^{(1)} \right\rangle \left\langle H^{(1)} \right\rangle$,

d. The next six correspond to interactions of the type $\left\langle H^{(1)} \right\rangle \left\langle H_q^{(2)} \right\rangle \left\langle H^{(1)} \right\rangle$,

e. The last 12 diagrams correspond to interactions of the type $\left\langle H^{(1)} \right\rangle \left\langle H^{(1)} \right\rangle \left\langle H^{(1)} \right\rangle \left\langle H^{(1)} \right\rangle$.

The above diagrams in Figure 14 are now used in the calculation of the matrix elements of equation (83).

Evaluation of Terms in Equation (83)

The terms in equation (83) are evaluated by considering the terms in the order in which they appear. The first term is given by

$$\Delta E\left(H_q^{(2)}\right) \equiv \sum_{\alpha' \neq \alpha} \frac{\left\langle \alpha \,\middle|\, H_q^{(2)} \,\middle|\, \alpha' \right\rangle \left\langle \alpha' \,\middle|\, H_q^{(2)} \,\middle|\, \alpha \right\rangle}{\left(E_\alpha^{(0)} - E_{\alpha'}^{(0)}\right)} \quad . \qquad (84)$$

Because this term corresponds to the electrostatic interaction between the two atoms, it has been considered previously by many authors [6,13]. The procedure used in evaluating this type of term is simply outlined, and the

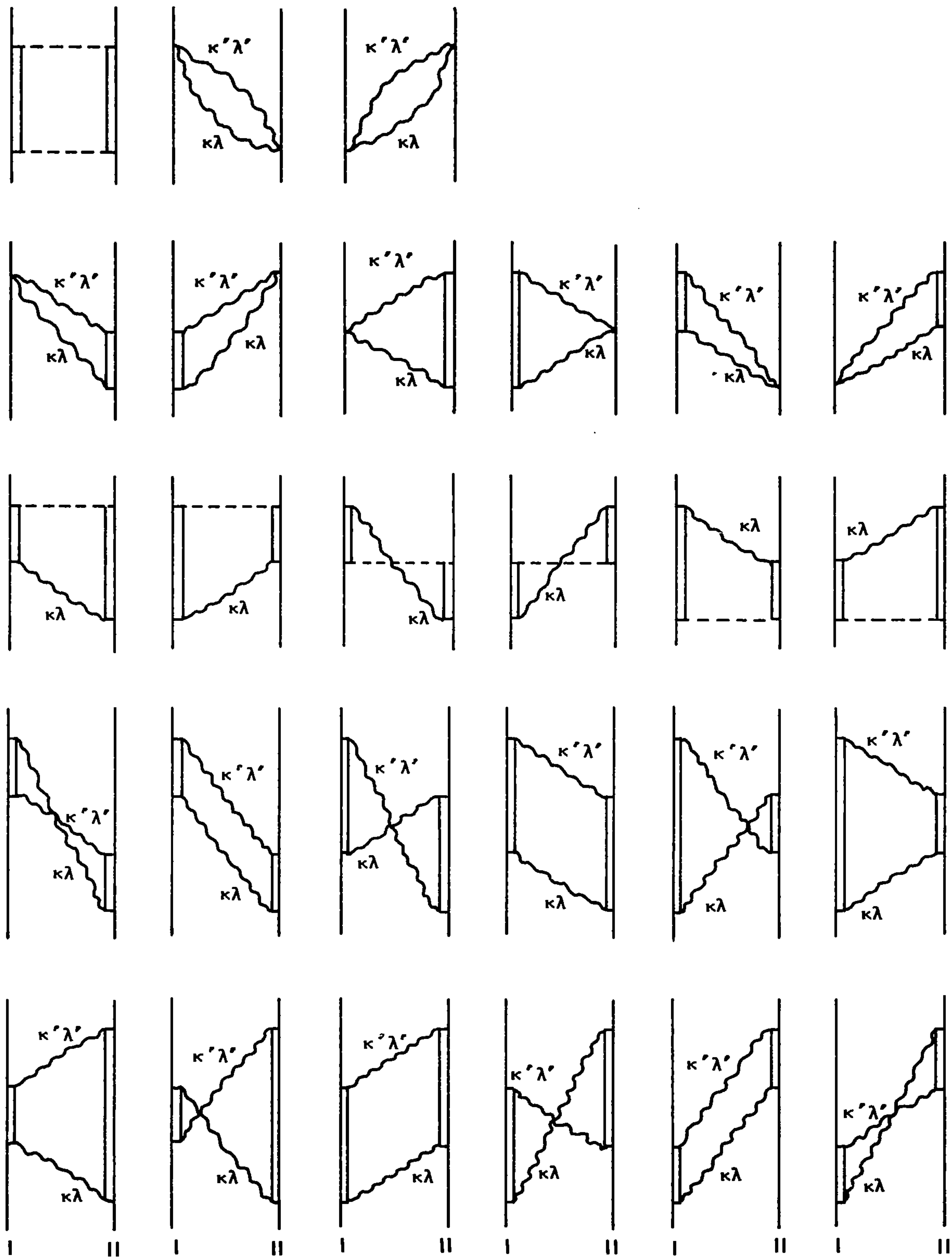


Figure 14. Interaction diagrams of equation (83).

result is given in terms of quantities used in this calculation. In evaluating quantities of the form given by equation (84), various techniques [12, 14] may be used to obtain approximate results since the exact evaluation is quite difficult. The usual approximation technique is known as the Unsöld Approximation [11], which consists of replacing the denominator of the quantity in equation (84) by a constant average energy $\bar{\epsilon}$. Once this is done the expression in equation (84) is evaluated by using the matrix summation rule over complete states. In this approximation, equation (84) reduces to

$$\Delta E\left(H_q^{(2)}\right) = \frac{1}{\bar{\epsilon}}\left\{\left\langle \alpha \left| \left[H_q^{(2)}\right]^2 \right| \alpha \right\rangle - \left[\left\langle \alpha \left| H_q^{(2)} \right| \alpha \right\rangle\right]^2\right\} .$$

An alternate approximation used in this calculation consists of restricting the intermediate atomic states to the 2-p states. Using this approximation (which, incidentally, is the same used by Casimir and Polder, and Power and Zienau), the expression in equation (84) becomes [15]

$$\Delta E\left(H_q^{(2)}\right) = \frac{1}{\left(E_\alpha^{(0)} - E_m^{(0)}\right)} \sum_m \left\langle \alpha \left| H_q^{(2)} \right| m \right\rangle \left\langle m \left| H_q^{(2)} \right| \alpha \right\rangle .$$

The factoring of the denominator from the sum over m is due to the fact that now the sum over m is just over the triply degenerate 2p states. Summing, the above expression reduces to

$$\Delta E\left(H_q^{(2)}\right) = \frac{1}{2\left(E_0 - E_1\right)} \left\langle \alpha \left| \left\{H_q^{(2)}\right\}^2 \right| \alpha \right\rangle .$$

Since the electrostatic interaction operator does not connect s-states, $\left(\left\langle \alpha \left| H_q^{(2)} \right| \alpha \right\rangle\right)^2$ vanishes when $\left|\alpha\right\rangle$ represents the 1s ground state. In this case both approximations yield the same result, if one lets $\bar{\epsilon} = 2\left(E_0 - E_1\right)$. In subsequent terms the latter approximation will be much easier to handle; even though, in the terms involving $H_q^{(2)}$, both approximations will again yield the same results with only a different constant.

Having introduced the approximation techniques to be used, one proceeds with the calculation of terms in equation (83). By substituting $H_q^{(2)}$ from equation (3) and factoring the atomic eigenstates as before, the preceding equation becomes

$$\Delta E\left(H_q^{(2)}\right) = \frac{16\pi^2}{2\left(E_0 - E_1\right)} \sum_{L,\ell,m} \sum_{\Gamma\gamma\mu} \frac{(-1)^{L+\Gamma}(L+\ell)!\,(\Gamma+\gamma)!}{R^{L+\ell+\Gamma+\gamma+1+1}}$$

$$\times \frac{\left\langle R_{1,0}(\mathrm{I}) \middle| r_1^{\ell+\gamma} \middle| R_{1,0}(\mathrm{I})\right\rangle \left\langle R_{1,0}(\mathrm{II}) \middle| r_2^{L+\Gamma} \middle| R_{1,0}(\mathrm{II})\right\rangle}{\left[(2\ell+1)(2L+1)(2\gamma+1)(2\Gamma+1)(\gamma-\mu)!(\gamma+\mu)!(\Gamma-\mu)!(\Gamma+\mu)!(\ell-m)!(\ell+m)!(L-m)!(L+m)!\right]^{1/2}}$$

$$\times \left\langle Y_0^0(\mathrm{I}) \middle| Y_\ell^{m^*}(\mathrm{I})\, Y_\gamma^{\mu^*}(\mathrm{I}) \middle| Y_0^0(\mathrm{I})\right\rangle \left\langle Y_0^0(\mathrm{II}) \middle| Y_L^{-m^*}(\mathrm{II})\, Y_\Gamma^{-\mu^*} \middle| Y_0^0(\mathrm{II})\right\rangle .$$

Using the coupling rule for Spherical Harmonics [10] and the result

$$\left\langle Y_{\ell_1}^{m_1} \middle| Y_\ell^{m^*}\, Y_\gamma^{\mu} \middle| Y_{\ell_1}^{m_1}\right\rangle = \frac{(-1)^m}{4\pi}\, \delta_{\ell,\gamma}\, \delta_{m,-\mu} \quad ,$$

the above simplifies to

$$\Delta E\left(H_q^{(2)}\right) = \sum_L \sum_\ell \sum_m \frac{(-1)^{2L}\left\{(L+\ell)!\right\}^2 \left\langle R_{1,0}(\mathrm{I}) \middle| r_1^{2\ell} \middle| R_{1,0}(\mathrm{I})\right\rangle \left\langle R_{1,0}(\mathrm{II}) \middle| r_2^{2L} \middle| R_{1,0}(\mathrm{II})\right\rangle}{2\left(E_0 - E_1\right) R^{2L+2\ell+2}\left[(2\ell+1)(2L+1)(\ell-m)!(\ell+m)!(L-m)!(L+m)!\right]} \qquad (85)$$

The radial matrix elements may be evaluated using the eigenfunctions defined by equation (21). The result is [16]

$$\left\langle R_{1,0}(\mathrm{I}) \middle| r_1^{2\ell} \middle| R_{1,0}(\mathrm{I})\right\rangle = \frac{(2\ell+2)!}{2}\left(\frac{a_0}{2Z_{\mathrm{I}}}\right)^{2\ell} . \qquad (86)$$

The expression in equation (85) will be used to obtain the various multipole contributions due to the electrostatic interaction energy. For example, if one wishes to obtain the dipole-dipole approximation, one lets $L = \ell = 1$ and sums over $m = +1, 0, -1$. This will be done later when one has the complete expression for ΔE.

The next term in equation (83) to be calculated may be redefined as[3]

$$\left\langle A \cdot A \right\rangle_{I} \left\langle A \cdot A \right\rangle_{II} \equiv \sum_{\alpha' \neq \alpha} \frac{\left\langle \alpha \middle| H_{I}^{(2)} \middle| \alpha' \right\rangle \left\langle \alpha' \middle| H_{II}^{(2)} \middle| \alpha \right\rangle}{\left(E_{\alpha}^{(0)} - E_{\alpha'}^{(0)} \right)} . \tag{87}$$

Expanding the above term, one gets

$$\begin{aligned} \left\langle A \cdot A \right\rangle_{I} \left\langle A \cdot A \right\rangle_{II} = \sum_{\alpha' \neq \alpha} \sum_{\alpha'' \neq \alpha} & \left(\frac{1}{\left\{ 2E_0 - \left[E_n(I) + E_m(II) + N\hbar c\kappa + N'\hbar c\kappa' \right] \right\}} \right) \\ & \times \left\langle I(0)\, II(0) \middle| \left\langle 0 \middle| H_{I}^{(2)} \middle| N_{\lambda}(\vec{\kappa}), \ldots N'_{\lambda'}(\vec{\kappa}'), \ldots \right\rangle \middle| I(n)\, II(m) \right\rangle \\ & \times \left\langle I(n)\, II(m) \middle| \left\langle N_{\lambda}(\vec{\kappa}), \ldots N'_{\lambda'}(\vec{\kappa}'), \ldots \middle| H_{II}^{(2)} \middle| 0 \right\rangle \middle| I(0)\, II(0) \right\rangle \end{aligned} \tag{88}$$

which can be simplified since $H_{I}^{(2)}$ depends only on the coordinates of atom I, and $H_{II}^{(2)}$ depends only on atom II.

To find the form of the intermediate photon states, one recalls that $H_{I,II}^{(2)}$ consist of four different products of field operators, as shown in equation (52). Using the relations given by equations (33) to (36), it can be seen that only one of these products can have a nonzero solution; that is

$$\begin{aligned} & \left\langle 0 \middle| a_{\lambda}(\vec{\kappa})\, a_{\lambda'}(\vec{\kappa}') \middle| N_{\lambda}(\vec{\kappa}), \ldots N'_{\lambda'}(\vec{\kappa}'), \ldots \right\rangle \\ & = \sqrt{N_{\lambda}(\vec{\kappa})}\, \sqrt{N'_{\lambda'}(\vec{\kappa}')} \left\langle 0 \middle| (N-1)_{\lambda}(\vec{\kappa}), \ldots (N-1)'_{\lambda'}(\vec{\kappa}'), \ldots \right\rangle , \end{aligned} \tag{89}$$

which is satisfied for the case in which $N = N' = 1$. Thus, the intermediate photon state may be given by $\left| 1_{\lambda}(\vec{\kappa}), \ldots 1_{\lambda'}(\vec{\kappa}'), \right\rangle$. An equally suitable

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3. This type of definition will be used throughout the remainder of this calculation. The form used indicates the type of operators associated with the various interactions.

solution is given by $\left| 1'_{\lambda'}(\vec{\kappa}'), \ldots 1_{\lambda}(\vec{\kappa}) \right\rangle$, which is obtained by interchanging the respective photon parameters. Thus, the most general solution is $(2)^{-1/2}\left\{ \left|\kappa\lambda;\kappa'\lambda'\right\rangle + \left|\kappa'\lambda';\kappa\lambda\right\rangle \right\}$. This intermediate photon state picks out one term corresponding to κ, λ and κ', λ' from $H^{(2)}_{I,II}$. Having established the form for the intermediate photon states, one evaluates the matrix products in equation (88) as follows:

Taking terms for $H^{(2)}_{I,II}$ that give nonzero results and substituting into the respective matrix products, one performs the indicated multiplications by using the approximations indicated before. Having done this, and having operated with the field operators, one obtains the following for equation (88):

$$\left\langle A \cdot A \right\rangle_{I} \left\langle A \cdot A \right\rangle_{II} = -\sum_{\kappa\lambda}\sum_{\kappa'\lambda'}\left[\frac{4\pi^2\hbar^2c^4}{4\mu^2c^2\,(\text{Vol.})^2c^2}\right]\left(\frac{1}{\kappa\kappa'}\right)\left[\frac{1}{\hbar c\,(\kappa+\kappa')}\right]\left(\frac{2}{\sqrt{2}}\right)\left(\frac{2}{\sqrt{2}}\right)$$
$$\times\left[\hat{\epsilon}_{\lambda}(\vec{\kappa})\cdot\hat{\epsilon}_{\lambda'}(\vec{\kappa}')\right]\left[\hat{\epsilon}_{\lambda}(\vec{\kappa})\cdot\hat{\epsilon}_{\lambda'}(\vec{\kappa}')\right]\left\langle I(0)\right| e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{\rho}_1}\left|I(0)\right\rangle\left\langle II(0)\right| e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{\rho}_2}\left|II(0)\right\rangle . \quad (90)$$

After rearrangement of the quantities and substitution of $\vec{\rho}_1$ and $\vec{\rho}_2$ in terms of the relations given in equation (47) and (48), one obtains

$$\left\langle A \cdot A \right\rangle_{I} \left\langle A \cdot A \right\rangle_{II} = -\left(\frac{2\pi^2\hbar}{\mu^2c^3\,\text{Vol.}^2}\right)\sum_{\kappa\lambda}\sum_{\kappa'\lambda'}\left[\frac{1}{\kappa\kappa'(\kappa+\kappa')}\right]\left[\hat{\epsilon}_{\lambda}(\vec{\kappa})\cdot\hat{\epsilon}_{\lambda'}(\vec{\kappa}')\right]\left[\hat{\epsilon}_{\lambda}(\vec{\kappa})\cdot\hat{\epsilon}_{\lambda'}(\vec{\kappa}')\right]$$
$$\times e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}\left\langle I(0)\right| e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}\left|I(0)\right\rangle\left\langle II(0)\right| e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}\left|II(0)\right\rangle \quad (91)$$

Before one can simplify the above result, one needs to replace the sums over $\vec{\kappa}$ and $\vec{\kappa}'$ by using the well-known substitution [17]

$$\sum_{\kappa} \rightarrow \int \frac{\text{Vol.}}{(2\pi)^3}\, d\vec{\kappa} = \frac{\text{Vol.}}{(2\pi)^3}\int \kappa^2 d\kappa \int d\Omega_{\kappa} \quad ,$$

where $(2\pi)^{-3}(\text{Vol.})$ is the density of individual states in $\vec{\kappa}$-space. Using the polarization relations given in Appendix A, equation (91) becomes

$$\left\langle A \cdot A \right\rangle_{I} \left\langle A \cdot A \right\rangle_{II} = -\left(\frac{\hbar}{2^5\pi^4\mu^2c^3}\right)\int d\vec{\kappa}\int d\vec{\kappa}'\left[\frac{1}{\kappa\kappa'(\kappa+\kappa')}\right]e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}\left[1+\cos^2(\hat{\kappa},\hat{\kappa}')\right] \quad (92)$$
$$\times\left\langle I(0)\right| e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}\left|I(0)\right\rangle\left\langle II(0)\right| e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}\left|II(0)\right\rangle \quad .$$

The preceding equation could have been obtained much easier by considering the interaction diagram in Figure 14 which corresponds to this term. If this had been done, steps required to show the form of the intermediate photon states could have been omitted since the interaction diagram shows that the intermediate state consists of two photons and that both atoms are in their respective initial states. Nevertheless, the answer would have been off by a factor of 2 since we would have neglected the possibility of interchanging κ' and κ.[4] This remark applies also to the third diagram of Figure 14 and to the next six diagrams that follow, since they too contain the $H^{(2)}_{I,II}$ operator which gives rise to instantaneous emission and absorption or absorption and emission of photons. Hence, each one of these diagrams corresponds to two possible modes which are indistinguishable and must be taken into account by taking linear combinations for the photon states as was done for the term just considered. A variation of this situation was discussed in conjunction with the remainder of the diagrams in Figure 14, in which there are two possible non-zero diagrams for each of the terms in equation (73) belonging to two possible unique ways to go from the initial state to the final state. Let us proceed to obtain the rest of the terms in equation (83) using a more direct approach.

The next term to be evaluated is very similar to the term just considered. This can be seen by referring to the third diagram of Figure 14 which corresponds to this term. The result is given by

$$\left\langle A \cdot A \right\rangle_{II} \left\langle A \cdot A \right\rangle_{I} = -\left(\frac{\hbar}{2^5 \pi^4 \mu^2 c^3}\right) \int d\vec{\kappa} \int d\vec{\kappa}' \left[\frac{1}{\kappa\kappa'(\kappa + \kappa')}\right] e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \left[1 + \cos^2(\hat{\kappa}, \hat{\kappa}')\right] \tag{93}$$

$$\times \left\langle II(0) \middle| e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} \middle| II(0) \right\rangle \left\langle I(0) \middle| e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1} \middle| I(0) \right\rangle ,$$

which is the same as the previous term, except that the exponentials have been replaced by their complex conjugates. Before computing the remainder of the terms in equation (83), the terms just evaluated are combined into a group. (The reason for this will be made clear later.) Combining equations (92) and (93), one defines

$$X(1) \equiv \left(\left\langle A \cdot A \right\rangle_{I} \left\langle A \cdot A \right\rangle_{II} + \left\langle A \cdot A \right\rangle_{II} \left\langle A \cdot A \right\rangle_{I} \right) ,$$

4. This point was discussed by correspondence with Prof. E. A. Power, London College.

where

$$X(1) = \left(\frac{-\hbar}{2^5 \pi^4 \mu^2 c^3}\right) \int d\vec{\kappa} \int d\vec{\kappa}' \left[\frac{1+\cos^2(\hat{\kappa},\hat{\kappa}')}{\kappa\kappa'(\kappa+\kappa')}\right] \left\{ e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1} \right\rangle \left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} \right\rangle + e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \left\langle e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} \right\rangle \left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1} \right\rangle \right\} . \tag{94}$$

The next term to be considered corresponds to the fourth diagram in Figure 14. This term is evaluated using the previous results and making use of the information contained in the interaction diagrams.

This term is defined as follows:

$$\left\langle A \cdot A \right\rangle_{I} \left\langle A \cdot P \right\rangle_{II} \left\langle A \cdot P \right\rangle_{II} = \sum_{\alpha'} \sum_{\alpha''} \frac{\left\langle H_I^{(2)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle}{\left(E_\alpha^{(0)} - E_{\alpha'}^{(0)}\right)\left(E_\alpha^{(0)} - E_{\alpha''}^{(0)}\right)} . \tag{95}$$

By referring to the interaction diagrams and substituting for the operators $H_I^{(2)}$ and $H_{II}^{(1)}$ only those terms which give nonzero results, one obtains

$$\begin{aligned}
\left\langle A\cdot A \right\rangle_{I} \left\langle A\cdot P \right\rangle_{II} \left\langle A\cdot P \right\rangle_{II} = & \sum_{\kappa\lambda} \sum_{\kappa'\lambda'} \sum_{m} \left\{ \frac{1}{\hbar c\,(\kappa+\kappa')\left[(E_1 - E_0) + \hbar c\kappa\right]} \right\} \left(\frac{2\pi\hbar}{\text{Vol.}}\right)^2 \left(\frac{1}{\hbar\mu^3 c^3}\right) \\
& \times \left\langle I(0)\ II(0) \right| \left\langle 0 \right| \left(\frac{1}{\kappa\kappa'}\right)^{1/2} \left[-a_\lambda(\vec{\kappa})\, a_{\lambda'}(\vec{\kappa}')\, e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{\rho}_1}\, \hat{\epsilon}_\lambda(\vec{\kappa})\cdot\hat{\epsilon}_{\lambda'}(\vec{\kappa}') \right] \left| \kappa\lambda, \kappa'\lambda' \right\rangle \left| I(0)\ II(0) \right\rangle \\
& \times \left\langle I(0)\ II(0) \right| \left\langle \kappa\lambda;\kappa'\lambda' \right| \left(\frac{1}{\kappa'}\right)^{1/2} \left[-a^{+}_{\lambda'}(\vec{\kappa}')\, e^{-i\vec{\kappa}'\cdot\vec{\rho}_2}\, \hat{\epsilon}_{\lambda'}(\vec{\kappa}')\cdot\vec{P}_{II}(\vec{r}_2) \right] \left| \kappa\lambda \right\rangle \left| I(0)\ II(m) \right\rangle \\
& \times \left\langle I(0)\ II(m) \right| \left\langle \kappa\lambda \right| \left(\frac{1}{\kappa}\right)^{1/2} \left[-a^{+}_{\lambda}(\vec{\kappa})\, e^{-i\vec{\kappa}\cdot\vec{\rho}_2}\, \hat{\epsilon}_{\lambda}(\vec{\kappa})\cdot\vec{P}_{II}(\vec{r}_2) \right] \left| 0 \right\rangle \left| I(0)\ II(0) \right\rangle
\end{aligned} \tag{96}$$

Operating on the photon states, substituting for $\vec{\rho}_1$ and $\vec{\rho}_2$ and rearranging terms, the above equation becomes

$$\begin{aligned}
\left\langle A\cdot A \right\rangle_{I} \left\langle A\cdot P \right\rangle_{II} \left\langle A\cdot P \right\rangle_{II} = & \sum_{\kappa\lambda} \sum_{\kappa'\lambda'} \sum_{m} \left[\frac{(2\pi\hbar)^2}{(\text{Vol.})^2 \hbar\mu^3 c^3}\right] \left\{ \frac{\left[\hat{\epsilon}_\lambda(\hat{\kappa})\cdot\hat{\epsilon}_{\lambda'}(\vec{\kappa}')\right] \sum_{ij} \left[\hat{\epsilon}_\lambda(\hat{\kappa})\right]_i \left[\hat{\epsilon}_{\lambda'}(\hat{\kappa}')\right]_j e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{\kappa\kappa'(\kappa+\kappa')\left[(E_1 - E_0) + \hbar c\kappa\right]} \right\} \\
& \times \left\langle I(0)\ II(0) \right| e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1} \left| I(0)\ II(0) \right\rangle \\
& \times \left\langle I(0)\ II(0) \right| e^{-i\vec{\kappa}'\cdot\vec{r}_2} \left[P_{II}(\vec{r}_2)\right]_i \left| I(0)\ II(m) \right\rangle \\
& \times \left\langle I(0)\ II(m) \right| e^{-i\vec{\kappa}\cdot\vec{r}_2} \left[\vec{P}_{II}(\vec{r}_2)\right]_j \left| I(0)\ II(0) \right\rangle .
\end{aligned} \tag{97}$$

The momentum operators may be replaced by position operators by making use of the well-known approximation [18]

$$\left\langle \ell \left| \vec{P} \right| m \right\rangle = \left\langle \ell \left| \frac{i\mu}{\hbar} (E_\ell - E_m) \vec{r} \right| m \right\rangle \quad . \tag{98}$$

Making this substitution, replacing the polarization products using results in Appendix A, summing over the atomic states, and replacing the sums over κ and κ', equation (97) becomes

$$\begin{aligned} \left\langle A\cdot A \right\rangle_{I} \left\langle A\cdot P \right\rangle_{II} \left\langle A\cdot P \right\rangle_{II} = & \left[\frac{(E_1 - E_0)^2}{2^4 \pi^4 \mu c^3 \hbar} \right] \int d\vec{\kappa} \int d\vec{\kappa'} \left(\frac{e^{-i(\vec{\kappa}+\vec{\kappa'})\cdot \vec{R}}}{\kappa\kappa'(\kappa+\kappa') \left[(E_1 - E_0) + \hbar c \kappa \right]} \right) \\ & \times \sum_{ij} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j - (\hat{\kappa}')_i (\hat{\kappa}')_j + (\hat{\kappa})_i (\hat{\kappa}')_j (\hat{\kappa}\cdot\hat{\kappa}') \right\} \\ & \times \left\langle I(0) \left| e^{i(\vec{\kappa}+\vec{\kappa'})\cdot \vec{r}_1} \right| I(0) \right\rangle \left\langle II(0) \left| e^{-i(\vec{\kappa}+\vec{\kappa'})\cdot \vec{r}_2} (\vec{r}_2)_i (\vec{r}_2)_j \right| II(0) \right\rangle \end{aligned} \tag{99}$$

The next term to be evaluated corresponds to the fifth diagram in Figure 14 and is defined by $\left\langle A\cdot A \right\rangle_{II} \left\langle A\cdot P \right\rangle_{I} \left\langle A\cdot P \right\rangle_{I}$. One notes that this term is identical in form to that given in equation (99) with atoms I and II interchanged. If the coordinates centered on atom I were replaced by those centered on atom II in equation (99), the result would not be correct unless the sign of the exponential factor containing the internuclear separation $\vec{R}$ is also changed. The necessity for this change is that interchanging atoms also requires the change of the direction of the vector $\vec{R}$, because the assumed convention calls for $\vec{R}$ to be directed from atom I to atom II. Hence, this term is given by

$$\begin{aligned} \left\langle A\cdot A \right\rangle_{II} \left\langle A\cdot P \right\rangle_{I} \left\langle A\cdot P \right\rangle_{I} = & \left[\frac{(E_1 - E_0)^2}{2^4 \pi^4 \mu c^3 \hbar} \right] \int d\vec{\kappa} \int d\vec{\kappa'} \left\{ \frac{e^{+i(\vec{\kappa}+\vec{\kappa'})\cdot \vec{R}}}{\kappa\kappa'(\kappa+\kappa') \left[(E_1 - E_0) + \hbar c \kappa \right]} \right\} \\ & \times \sum_{ij} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j - (\hat{\kappa}')_i (\hat{\kappa}')_j + (\hat{\kappa})_i (\hat{\kappa}')_j (\hat{\kappa}\cdot\hat{\kappa}') \right\} \\ & \times \left\langle I(0) \left| e^{-i(\vec{\kappa}+\vec{\kappa'})\cdot \vec{r}_1} (\vec{r}_1)_i (\vec{r}_1)_j \right| I(0) \right\rangle \left\langle II(0) \left| e^{i(\vec{\kappa}+\vec{\kappa'})\cdot \vec{r}_2} \right| II(0) \right\rangle \quad . \end{aligned} \tag{100}$$

The next term to be evaluated corresponds to the sixth diagram in Figure 14 and is defined by $\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot A\right\rangle_{I}\left\langle A\cdot P\right\rangle_{II}$. Using the interaction diagram corresponding to this term, and performing similar operations as for previous terms, one obtains

$$\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot A\right\rangle_{I}\left\langle A\cdot P\right\rangle_{II} = \sum_{\kappa\lambda}\sum_{\kappa'\lambda'}\sum_{m}\left[\frac{(2\pi\hbar)^2}{\text{Vol.}^2\hbar\mu^3c^3}\right]\left\{\frac{1}{\kappa\kappa'\left[(E_1-E_0)+\hbar c\kappa\right]\left[(E_1-E_0)+\hbar c\kappa'\right]}\right\}$$
$$\times\left\langle I(0)\ II(0)\right|\left\langle 0\right|\ \mathcal{a}_{\lambda'}(\vec{\kappa}')\ e^{i\vec{\kappa}'\cdot\vec{\rho}_2}\ \hat{\epsilon}_{\lambda'}(\vec{\kappa}')\cdot\vec{P}_{II}(\vec{r}_2)\ \left|\kappa'\lambda'\right\rangle\left|I(0)\ II(m)\right\rangle$$
$$\times\left\langle I(0)\ II(m)\right|\left\langle\kappa'\lambda'\right|\ \mathcal{a}_{\lambda}(\vec{\kappa})\mathcal{a}^{+}_{\lambda'}(\vec{\kappa}')\ e^{i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{\rho}_1}\ \hat{\epsilon}_{\lambda}(\hat{\kappa})\cdot\hat{\epsilon}_{\lambda'}(\hat{\kappa}')\ \left|\kappa\lambda\right\rangle\left|I(0)\ II(m)\right\rangle$$
$$\times\left\langle I(0)\ II(m)\right|\left\langle\kappa\lambda\right|\ -\mathcal{a}^{+}_{\lambda}(\vec{\kappa})\ e^{-i(\vec{\kappa}\cdot\vec{\rho}_2)}\ \hat{\epsilon}_{\lambda}(\vec{\kappa})\cdot\vec{P}_{II}(\vec{r}_2)\ \left|0\right\rangle\left|I(0)\ II(0)\right\rangle \quad . \tag{101}$$

The form of this term is very instructive in that one sees quite clearly that a term with κ,λ and κ',λ' interchanged is also a possible combination. Thus, even though the intermediate photon states are not made up of linear combinations of $\kappa,\lambda;\ \kappa',\lambda'$, one still has two possible modes due to the instantaneous emission and absorption process associated with the $H_I^{(2)}$ operator. Performing similar operations as before, equation (101) becomes

$$\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot A\right\rangle_{I}\left\langle A\cdot P\right\rangle_{II} = \left[\frac{(E_1-E_0)^2}{2^4\pi^4\mu c^2}\right]\int\frac{d\vec{\kappa}}{\kappa}\int\frac{d\vec{\kappa}'}{\kappa'}\left\{\frac{e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1-E_0)+\hbar c\kappa\right]\left[(E_1-E_0)+\hbar c\kappa'\right]}\right\}$$
$$\times\sum_{ij}\left\{\delta_{ij}-(\hat{\kappa})_i(\hat{\kappa})_j-(\hat{\kappa}')_i(\hat{\kappa}')_j+(\hat{\kappa})_i(\hat{\kappa}')_j(\hat{\kappa}\cdot\hat{\kappa}')\right\} \tag{102}$$
$$\times\left\langle I(0)\right|\ e^{i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_1}\ \left|I(0)\right\rangle\left\langle II(0)\right|\ e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_2}\ (\vec{r}_2)_i(\vec{r}_2)_j\ \left|II(0)\right\rangle$$

The next term is obtained directly from this result and is given by

$$\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot A\right\rangle_{II}\left\langle A\cdot P\right\rangle_{I} = \left[\frac{(E_1 - E_0)^2}{2^4\pi^4\mu c^2}\right]\int\frac{d\vec{\kappa}}{\kappa}\int\frac{d\vec{\kappa}'}{\kappa'}\left\{\frac{e^{+i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c\kappa\right]\left[(E_1 - E_0) + \hbar c\kappa'\right]}\right\}$$

$$\times\sum_{ij}\left\{\delta_{ij} - (\hat{\kappa})_i(\hat{\kappa})_j - (\hat{\kappa}')_i(\hat{\kappa}')_j + (\hat{\kappa})_i(\hat{\kappa}')_j(\hat{\kappa}\cdot\hat{\kappa}')\right\}$$

$$\times\left\langle I(0)\right|e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\left|I(0)\right\rangle\left\langle II(0)\right|e^{i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_2}\left|II(0)\right\rangle \quad . \qquad (103)$$

The next term corresponds to the eighth term in Figure 14 and is defined by $\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot A\right\rangle_{II}$. Carrying out similar operations and simplifications as above, this term reduces to

$$\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot A\right\rangle_{II} = \left[\frac{(E_1 - E_0)^2}{2^4\pi^4\mu c^3\hbar}\right]\int\frac{d\vec{\kappa}}{\kappa}\int\frac{d\vec{\kappa}'}{\kappa'}\left\{\frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa + \kappa')\left[(E_1 - E_0) + \hbar c\kappa'\right]}\right\}$$

$$\times\sum_{ij}\left\{\delta_{ij} - (\hat{\kappa})_i(\hat{\kappa})_j - (\hat{\kappa}')_i(\hat{\kappa}')_j + (\hat{\kappa})_i(\hat{\kappa}')_j(\hat{\kappa}\cdot\hat{\kappa}')\right\}$$

$$\times\left\langle I(0)\right|e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\left|I(0)\right\rangle\left\langle II(0)\right|e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}\left|II(0)\right\rangle \quad . \qquad (104)$$

The above quantity could also have been obtained from equation (100) by taking the complex conjugate of that expression and reordering the various matrix products, provided one notes the interchange of intermediate states α' and α''. Otherwise, the denominator of the expression in equation (104) would be in error.

The next term to be calculated corresponds to the ninth diagram in Figure 14 and is defined by $\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot A\right\rangle_{I}$. Comparison with equation (104) shows that this term may be evaluated using the previous method of interchanging the atomic coordinate systems. When this is done, the above term becomes

$$\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot A\right\rangle_{I} = \left[\frac{(E_1-E_0)^2}{2^4\pi^4\mu c^3\hbar}\right]\int\frac{d\vec{\kappa}}{\kappa}\int\frac{d\vec{\kappa}'}{\kappa'}\left\{\frac{e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa+\kappa')\left[(E_1-E_0)+\hbar c\kappa'\right]}\right\}$$

$$\times\sum_{ij}\left\{\delta_{ij}-(\hat{\kappa})_i(\hat{\kappa})_j-(\hat{\kappa}')_i(\hat{\kappa}')_j+(\hat{\kappa})_i(\hat{\kappa}')_j(\hat{\kappa}\cdot\hat{\kappa}')\right\}$$

$$\times\left\langle I(0)\left|e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}\right|I(0)\right\rangle\left\langle II(0)\left|e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}(\vec{r}_2)_i(\vec{r}_2)_j\right|II(0)\right\rangle \tag{105}$$

Before proceeding to the next term, one notes that the basic differences in the last six terms just evaluated occur in the energy denominators, the exponential factor in R, and the matrix products over atoms I and II. Combining equations (99), (100), (102), (103), (104), and (105), one obtains an expression for this group of terms which is defined as follows:

$$X(2) \equiv \Big(\left\langle A\cdot A\right\rangle_{I}\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot P\right\rangle_{II}+\left\langle A\cdot A\right\rangle_{II}\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot P\right\rangle_{I}+\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot A\right\rangle_{I}\left\langle A\cdot P\right\rangle_{II}$$
$$+\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot A\right\rangle_{II}\left\langle A\cdot P\right\rangle_{I}+\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot A\right\rangle_{II}+\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot A\right\rangle_{I}\Big)$$

where

$$X(2) = \left[\frac{(E_1-E_0)^2}{2^4\pi^4\mu c^3\hbar}\right]\int\frac{d\vec{\kappa}}{\kappa}\int\frac{d\vec{\kappa}'}{\kappa'}\sum_{ij}\left\{\delta_{ij}-(\hat{\kappa})_i(\hat{\kappa})_j-(\hat{\kappa}')_i(\hat{\kappa}')_j+(\hat{\kappa})_i(\hat{\kappa}')_j(\hat{\kappa}\cdot\hat{\kappa}')\right\}$$

$$\times\left\{\frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa+\kappa')\left[(E_1-E_0)+\hbar c\kappa\right]}\left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}\right\rangle\left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}(\vec{r}_2)_i(\vec{r}_2)_j\right\rangle\right.$$

$$+\frac{e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa+\kappa')\left[(E_1-E_0)+\hbar c\kappa\right]}\left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}\right\rangle$$

$$+\frac{\hbar c\, e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1-E_0)+\hbar c\kappa\right]\left[(E_1-E_0)+\hbar c\kappa'\right]}\left\langle e^{+i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_1}\right\rangle\left\langle e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_2}(\vec{r}_2)_i(\vec{r}_2)_j\right\rangle$$

$$+\frac{\hbar c\, e^{+i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1-E_0)+\hbar c\kappa\right]\left[(E_1-E_0)+\hbar c\kappa'\right]}\left\langle e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle e^{+i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_2}\right\rangle$$

$$+\frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa+\kappa')\left[(E_1-E_0)+\hbar c\kappa'\right]}\left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}\right\rangle$$

$$\left.+\frac{e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa+\kappa')\left[(E_1-E_0)+\hbar c\kappa'\right]}\left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}\right\rangle\left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}(\vec{r}_2)_i(\vec{r}_2)_j\right\rangle\right\} \tag{106}$$

In this term, the matrix elements are to be taken over the appropriate eigenstates. In subsequent discussions this group of terms will be referred to simply as $X(2)$.

The next term of equation (83) to be considered corresponds to the tenth diagram of Figure 14. This is the first of a group of six terms corresponding to the third row of diagrams in Figure 14. Due to the great number of operations involved in obtaining each term, only the first term in this group will be evaluated in some detail. After this is done, the results of the other terms within this group will be expressed as a sum of terms defined by $X(3)$. Let this term be defined by

$$\left\langle H_q \right\rangle \left\langle A\cdot P \right\rangle_{I} \left\langle A\cdot P \right\rangle_{II} \equiv \sum_{\alpha'} \sum_{\alpha''} \frac{\left\langle H_q^{(2)} \right\rangle \left\langle H_I^{(1)} \right\rangle \left\langle H_{II}^{(1)} \right\rangle}{\left(E_\alpha^{(0)} - E_{\alpha'}^{(0)}\right)\left(E_\alpha^{(0)} - E_{\alpha''}^{(0)}\right)} \quad . \tag{107}$$

Expanding this expression and substituting for the operators $H_I^{(1)}$, $H_{II}^{(1)}$ only the factors which give nonzero results, the above expression becomes

$$\begin{aligned} \left\langle H_q \right\rangle \left\langle A\cdot P \right\rangle_{I} \left\langle A\cdot P \right\rangle_{II} = \sum_{\kappa\lambda} \sum_{m} \Bigg\{ & \frac{1}{\left[(E_1 - E_0) + \hbar c \kappa\right]\left[2(E_1 - E_0)\right]} \\ & \times \left\langle I(0)\ II(0) \right| \left\langle 0 \right| H_q^{(2)} \left| 0 \right\rangle \left| I(m)\ II(m) \right\rangle \\ & \times \left\langle I(m)\ II(m) \right| \left\langle 0 \right| \left(-\frac{1}{\mu i}\right) \sqrt{\frac{2\pi\hbar}{\mathrm{Vol.}}} \left(\frac{1}{c\kappa}\right)^{1/2} \left[a_\lambda(\vec{\kappa})\, e^{i\vec{\kappa}\cdot\vec{\rho}_1}\, \hat{\epsilon}_\lambda(\vec{\kappa})\cdot\vec{P}_I(r_1) \right] \left| \kappa\lambda \right\rangle \left| I(0)\ II(m) \right\rangle \\ & \times \left\langle I(0)\ II(m) \right| \left\langle \kappa\lambda \right| \left(-\frac{1}{\mu i}\right) \sqrt{\frac{2\pi\hbar}{\mathrm{Vol.}}} \left(\frac{1}{c\kappa}\right)^{1/2} \left[-a_\lambda^{+}(\vec{\kappa})\, e^{-i\vec{\kappa}\cdot\vec{\rho}_2}\, \hat{\epsilon}_\lambda(\vec{\kappa})\cdot\vec{P}_{II}(r_2) \right] \left| 0 \right\rangle \left| I(0)\ II(0) \right\rangle \Bigg\} . \end{aligned}$$

Operating on the photon states, collecting terms, substituting for the momenta using equation (98), replacing $\vec{\rho}_1$ and $\vec{\rho}_2$ in terms of $\vec{R}$, summing over atomic states, replacing the sum over κ by its corresponding integral, and substituting for the polarization relations using the results of Appendix A, the above expression becomes

$$\left\langle H_q \right\rangle \left\langle A\cdot P \right\rangle_{I} \left\langle A\cdot P \right\rangle_{II} = \left[-\frac{(E_1 - E_0)^2}{2^3 \pi^2 \hbar^3 c^3} \right] \int \frac{d\vec{\kappa}}{\kappa} \frac{e^{-i\vec{\kappa}\cdot\vec{R}} \sum_{ij} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j \right\}}{\left[(E_1 - E_0) + \hbar c\kappa\right]\left[E_1 - E_0\right]} \tag{108}$$

$$\times \left\langle H_q^{(2)}\, e^{i\vec{\kappa}\cdot\vec{r}_1} (\vec{r}_1)_i\, e^{-i\vec{\kappa}\cdot\vec{r}_2} (\vec{r}_2)_j \right\rangle \quad .$$

Performing similar operations on the next five terms and using similar definitions, one can combine these terms as follows:

$$X(3) \equiv \Big(\left\langle H_q^{(2)} \right\rangle \left\langle A\cdot P \right\rangle_{I} \left\langle A\cdot P \right\rangle_{II} + \left\langle H_q^{(2)} \right\rangle \left\langle A\cdot P \right\rangle_{II} \left\langle A\cdot P \right\rangle_{I} + \left\langle A\cdot P \right\rangle_{I} \left\langle H_q^{(2)} \right\rangle \left\langle A\cdot P \right\rangle_{II}$$

$$\left\langle A\cdot P \right\rangle_{II} \left\langle H_q^{(2)} \right\rangle \left\langle A\cdot P \right\rangle_{I} + \left\langle A\cdot P \right\rangle_{I} \left\langle A\cdot P \right\rangle_{II} \left\langle H_q^{(2)} \right\rangle + \left\langle A\cdot P \right\rangle_{II} \left\langle A\cdot P \right\rangle_{I} \left\langle H_q^{(2)} \right\rangle \Big) ,$$

where

$$X(3) = \left[- \frac{(E_1 - E_0)^2}{2^3 \pi^2 \hbar^3 c^3} \right] \int \frac{d\vec{\kappa}}{\kappa} \sum_{ij} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j \right\}$$

$$\times \Bigg\{ \frac{e^{-i\vec{\kappa}\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c \kappa \right] \left[E_1 - E_0 \right]} \left\langle H_q^{(2)} \, e^{i\vec{\kappa}\cdot\vec{r}_1} (\vec{r}_1)_i \, e^{-i\vec{\kappa}\cdot\vec{r}_2} (\vec{r}_2)_j \right\rangle$$

$$+ \frac{e^{+i\vec{\kappa}\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c \kappa \right] \left[E_1 - E_0 \right]} \left\langle H_q^{(2)} \, e^{-i\vec{\kappa}\cdot\vec{r}_1} (\vec{r}_1)_i \, e^{+i\vec{\kappa}\cdot\vec{r}_2} (\vec{r}_2)_j \right\rangle$$

$$+ \frac{-2e^{-i\vec{\kappa}\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c \kappa \right] \left[(E_1 - E_0) + \hbar c \kappa \right]} \left\langle e^{+i\vec{\kappa}\cdot\vec{r}_1} (\vec{r}_1)_i \, H_q^{(2)} \, e^{-i\vec{\kappa}\cdot\vec{r}_2} (\vec{r}_2)_j \right\rangle$$

$$+ \frac{-2e^{+i\vec{\kappa}\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c \kappa \right] \left[(E_1 - E_0) + \hbar c \kappa \right]} \left\langle e^{-i\vec{\kappa}\cdot\vec{r}_1} (\vec{r}_1)_i \, H_q^{(2)} \, e^{+i\vec{\kappa}\cdot\vec{r}_2} (\vec{r}_2)_j \right\rangle$$

$$+ \frac{e^{-i\vec{\kappa}\cdot\vec{R}}}{\left[(E_1 - E_0) \right] \left[(E_1 - E_0) + \hbar c \kappa \right]} \left\langle e^{+i\vec{\kappa}\cdot\vec{r}_1} (\vec{r}_1)_i \, e^{-i\vec{\kappa}\cdot\vec{r}_2} (\vec{r}_2)_j \, H_q^{(2)} \right\rangle$$

$$+ \frac{e^{+i\vec{\kappa}\cdot\vec{R}}}{\left[(E_1 - E_0) \right] \left[(E_1 - E_0) + \hbar c \kappa \right]} \left\langle e^{-i\vec{\kappa}\cdot\vec{r}_1} (\vec{r}_1)_i \, e^{+i\vec{\kappa}\cdot\vec{r}_2} (\vec{r}_2)_j \, H_q^{(2)} \right\rangle \Bigg\} .$$

(109)

The above group of terms shows, in a systematic manner, the way the field operators and the electrostatic potential are coupled to produce nonzero contributions to the interaction energy. These terms will be discussed later in more detail, by expressing the operator $H_q^{(2)}$ in terms of $\vec{r}_1$ and $\vec{r}_2$, and $e^{i\vec{\kappa}\cdot\vec{r}}$ expanded in a power series.

The remainder of the terms in equation (83) to be evaluated correspond to terms involving products of $H^{(1)}_{I,II}$. They are illustrated by the last 12 diagrams of Figure 14. These terms have several common factors and will be combined into a group as before. Since the number of steps required to evaluate each of the 12 terms is rather large, only the first term of this group will be evaluated in some detail. The evaluation of subsequent terms is done in a similar manner with only minor deviations. Let this term be defined by

$$\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot P\right\rangle_{II}$$

$$\equiv \sum_{\alpha'}\sum_{\alpha''}\sum_{\alpha'''}\frac{\left\langle H^{(1)}_{I}\right\rangle\left\langle H^{(1)}_{I}\right\rangle\left\langle H^{(1)}_{II}\right\rangle\left\langle H^{(1)}_{II}\right\rangle}{\left(E^{(0)}_{\alpha}-E^{(0)}_{\alpha'}\right)\left(E^{(0)}_{\alpha}-E^{(0)}_{\alpha''}\right)\left(E^{(0)}_{\alpha}-E^{(0)}_{\alpha'''}\right)}\quad . \tag{110}$$

Using the interaction diagrams to obtain the form of the intermediate states, and substituting for the operators $H^{(1)}_{I,II}$, only those factors which give nonzero results, equation (110) becomes

$$\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot P\right\rangle_{I}\left\langle A\cdot P\right\rangle_{II}\left\langle A\cdot P\right\rangle_{II}$$

$$= \sum_{\alpha'}\sum_{\alpha''}\sum_{\alpha'''}\left\{\frac{1}{\left[2E_0-(E_1+E_0+\hbar c\kappa)\right]\left[2E_0-(2E_0+\hbar c\kappa+\hbar c\kappa')\right]\left[2E_0-(E_1+E_0+\hbar c\kappa)\right]}\right\}$$

$$\times\left\langle I(0)\ II(0)\right|\left\langle 0\right|\left(-\frac{1}{i\mu}\right)\sqrt{\frac{2\pi\hbar}{\text{Vol.}}}\left(\frac{1}{c\kappa}\right)^{1/2}\left[a_{\lambda}(\vec{\kappa})\,e^{i\vec{\kappa}\cdot\vec{\rho}_1}\,\hat{\epsilon}_{\lambda}(\vec{\kappa})\cdot\vec{P}_{I}(\vec{r}_1)\right]\left|\kappa\lambda\right\rangle\left|I(m)\ II(0)\right\rangle$$

$$\times\left\langle I(m)\ II(0)\right|\left\langle\kappa\lambda\right|\left(-\frac{1}{i\mu}\right)\sqrt{\frac{2\pi\hbar}{\text{Vol.}}}\left(\frac{1}{c\kappa'}\right)^{1/2}\left[a_{\lambda'}(\vec{\kappa}')\,e^{i\vec{\kappa}'\cdot\vec{\rho}_1}\,\hat{\epsilon}_{\lambda'}(\vec{\kappa}')\cdot\vec{P}_{I}(\vec{r}_1)\right]\left|\kappa\lambda,\kappa'\lambda'\right\rangle\left|I(0)\ II(0)\right\rangle$$

$$\times\left\langle I(0)\ II(0)\right|\left\langle\kappa\lambda,\kappa'\lambda'\right|\left(-\frac{1}{i\mu}\right)\sqrt{\frac{2\pi\hbar}{\text{Vol.}}}\left(\frac{1}{c\kappa'}\right)^{1/2}\left[-a^{+}_{\lambda'}(\vec{\kappa}')\,e^{-i\vec{\kappa}'\cdot\vec{\rho}_2}\,\hat{\epsilon}_{\lambda'}(\vec{\kappa}')\cdot\vec{P}_{II}(\vec{r}_2)\right]\left|\kappa\lambda\right\rangle\left|I(0)\ II(m)\right\rangle$$

$$\times\left\langle I(0)\ II(m)\right|\left\langle\kappa\lambda\right|\left(-\frac{1}{i\mu}\right)\sqrt{\frac{2\pi\hbar}{\text{Vol.}}}\left(\frac{1}{c\kappa}\right)^{1/2}\left[-a^{+}_{\lambda}(\vec{\kappa})\,e^{-i\vec{\kappa}\cdot\vec{\rho}_2}\,\hat{\epsilon}_{\lambda}(\vec{\kappa})\cdot\vec{P}_{II}(\vec{r}_2)\right]\left|0\right\rangle\left|I(0)\ II(0)\right\rangle\quad . \tag{111}$$

Collecting terms, operating on the photon states, substituting for $\vec{\rho}_1$ and $\vec{\rho}_2$, replacing the momentum operators, substituting for the polarization sums from Appendix A, replacing the sums over κ and κ', and summing over the atomic intermediate states, the above expression reduces to

$$\langle A\cdot P\rangle_{I}\langle A\cdot P\rangle_{I}\langle A\cdot P\rangle_{II}\langle A\cdot P\rangle_{II}$$

$$= \left[-\frac{(E_1 - E_0)^4}{2^4 \pi^4 \hbar^3 c^3}\right] \int \frac{d\vec{\kappa}}{\kappa} \int \frac{d\vec{\kappa}'}{\kappa'} \left\{ \frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c\kappa\right]\left[\kappa + \kappa'\right]\left[(E_1 - E_0) + \hbar c\kappa\right]} \right\}$$

$$\times \sum_{i,j} \sum_{\ell,s} \left\{\delta_{is} - (\hat{\kappa})_i(\hat{\kappa})_s\right\}\left\{\delta_{j\ell} - (\hat{\kappa}')_j(\hat{\kappa}')_\ell\right\}$$

$$\times \left\langle I(0)\right| e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1} (\vec{r}_1)_i (\vec{r}_1)_j \left|I(0)\right\rangle$$

$$\times \left\langle II(0)\right| e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_\ell (\vec{r}_2)_s \left|II(0)\right\rangle \quad . \tag{112}$$

The remainder of the terms in this group are obtained in a similar manner with only minor modifications. Defining this group of terms as X(4), one can write the results as follows:

$$X(4) = \left[-\frac{(E_1 - E_0)^4}{2^4 \pi^4 \hbar^2 c^2}\right] \int \frac{d\vec{\kappa}}{\kappa} \int \frac{d\vec{\kappa}'}{\kappa'} \sum_{i,j} \sum_{\ell,s} \left\{\delta_{is} - (\hat{\kappa})_i(\hat{\kappa})_s\right\}\left\{\delta_{j\ell} - (\hat{\kappa}')_j(\hat{\kappa}')_\ell\right\}$$

$$\times \left\{ \frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1} (\vec{r}_1)_i (\vec{r}_1)_j\right\rangle \left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_\ell (\vec{r}_2)_s\right\rangle}{\left[(E_1 - E_0) + \hbar c\kappa\right]\left[\hbar c\kappa + \hbar c\kappa'\right]\left[(E_1 - E_0) + \hbar c\kappa\right]} \right.$$

$$+ \frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1} (\vec{r}_1)_i (\vec{r}_1)_j\right\rangle \left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_\ell (\vec{r}_2)_s\right\rangle}{\left[(E_1 - E_0) + \hbar c\kappa'\right]\left[\hbar c\kappa + \hbar c\kappa'\right]\left[(E_1 - E_0) + \hbar c\kappa\right]}$$

$$+ \frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \left\langle e^{+i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_1} (\vec{r}_1)_i (\vec{r}_1)_j\right\rangle \left\langle e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_\ell (\vec{r}_2)_s\right\rangle}{\left[(E_1 - E_0) + \hbar c\kappa\right]\left[(E_1 - E_0) + (E_1 - E_0) + \hbar c\kappa + \hbar c\kappa'\right]\left[(E_1 - E_0) + \hbar c\kappa\right]}$$

$$+ \frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \left\langle e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1} (\vec{r}_1)_i (\vec{r}_1)_j\right\rangle \left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_\ell (\vec{r}_2)_s\right\rangle}{\left[(E_1 - E_0) + \hbar c\kappa\right]\left[(E_1 - E_0) + (E_1 - E_0)\right]\left[(E_1 - E_0) + \hbar c\kappa'\right]}$$

$$
+\frac{e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}\left\langle e^{+i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_2}(\vec{r}_2)_\ell(\vec{r}_2)_s\right\rangle}{\left[(E_1-E_0)+\hbar c\kappa'\right]\left[(E_1-E_0)+(E_1-E_0)+\hbar c\kappa+\hbar c\kappa'\right]\left[(E_1-E_0)+\hbar c\kappa\right]}
$$

$$
+\frac{e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}\left\langle e^{i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_2}(\vec{r}_2)_\ell(\vec{r}_2)_s\right\rangle}{\left[(E_1-E_0)+\hbar c\kappa\right]\left[(E_1-E_0)+(E_1-E_0)\right]\left[(E_1-E_0)+\hbar c\kappa'\right]}
$$

$$
+\frac{e^{+i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}\left\langle e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle e^{i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_2}(\vec{r}_2)_\ell(\vec{r}_2)_s\right\rangle}{\left[(E_1-E_0)+\hbar c\kappa'\right]\left[(E_1-E_0)+(E_1-E_0)\right]\left[(E_1-E_0)+\hbar c\kappa\right]}
$$

$$
+\frac{e^{+i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}\left\langle e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle e^{+i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_2}(\vec{r}_2)_\ell(\vec{r}_2)_s\right\rangle}{\left[(E_1-E_0)+\hbar c\kappa\right]\left[(E_1-E_0)+(E_1-E_0)+\hbar c\kappa+\hbar c\kappa'\right]\left[(E_1-E_0)+\hbar c\kappa'\right]}
$$

$$
+\frac{e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}\left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}(\vec{r}_2)_\ell(\vec{r}_2)_s\right\rangle}{\left[(E_1-E_0)+\hbar c\kappa\right]\left[(E_1-E_0)+(E_1-E_0)\right]\left[(E_1-E_0)+\hbar c\kappa'\right]}
$$

$$
+\frac{e^{+i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}\left\langle e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle e^{+i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_2}(\vec{r}_2)_\ell(\vec{r}_2)_s\right\rangle}{\left[(E_1-E_0)+\hbar c\kappa\right]\left[(E_1-E_0)+(E_1-E_0)+\hbar c\kappa+\hbar c\kappa'\right]\left[(E_1-E_0)+\hbar c\kappa\right]}
$$

$$
+\frac{e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}\left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}(\vec{r}_2)_\ell(\vec{r}_2)_s\right\rangle}{\left[(E_1-E_0)+\hbar c\kappa\right]\left[\hbar c\kappa+\hbar c\kappa'\right]\left[(E_1-E_0)+\hbar c\kappa'\right]}
$$

$$
+\frac{e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}\left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}(\vec{r}_2)_\ell(\vec{r}_2)_s\right\rangle}{\left[(E_1-E_0)+\hbar c\kappa\right]\left[\hbar c\kappa+\hbar c\kappa'\right]\left[(E_1-E_0)+\hbar c\kappa\right]} \tag{113}
$$

The above terms are listed in the same order as the corresponding diagrams of Figure 14. The reason for expressing the denominators in this manner is to indicate explicitly the intermediate state energy denominators and to keep track on the various terms. A check may be made on the exponential factors and energy denominators by comparing the first and last terms in equation (113). One should be able to obtain the exponential factors of the last term by taking complex conjugates of the imaginary factors in the first term. The remainder of the terms may be checked in a similar manner.

Combining the above results, the interaction energy correction $\Delta E/e^4$ is given by

$$\Delta E/e^4 = \Delta E(H_q) + X(1) + X(2) + X(3) + X(4) \quad , \tag{114}$$

where the above quantities are defined by equations (85), (94), (106), (109), and (113). Note that to this point the only approximation one has made involves restricting the intermediate atomic states to the 2p levels; otherwise, the above result is good to all multipole orders both in the electrostatic potential and the radiation field. The various approximations will be examined in subsequent discussions.

DIPOLE-DIPOLE APPROXIMATIONS

Approximations to the Interaction Energy

The results obtained in the preceding discussion are used in recombining the individual groups given by equation (114) into a form suitable for subsequent approximations. The dipole approximation will be applied and the results compared to those of Casimir and Polder. The results will be given in terms of corrections to the interaction energy due to only the electrostatic interaction. In the dipole-dipole approximation this will consist of taking the terms corresponding to $L_1 = L_2 = 1$, and $M = +1, 0, -1$ in the expression for $H_q^{(2)}$ in equation (3) and setting the exponential terms $e^{i\vec{\kappa}\cdot\vec{r}}$ equal to unity in the various matrix elements in equation (114). Since higher approximations will be considered later, the initial results will be put in a form suitable for use in subsequent applications.

The terms in equation (114) will be evaluated in the order in which they appear. The first term is already in the form desired; hence, it need not be considered. The next term $X(1)$ is defined in equation (94). Interchanging the coordinates for atoms I and II, and substituting for the volume element $d\vec{\kappa}$ in terms of $\kappa^2 d\kappa d\Omega_\kappa$, $X(1)$ becomes

$$X(1) = \left(-\frac{2K}{2^5\pi^4\mu^2c^3}\right)\int_0^\infty \kappa^2 d\kappa \int_{4\pi} d\Omega\kappa \int_0^\infty \kappa'^2 d\kappa' \int_{4\pi} d\Omega\kappa' \, \frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}\left\{1+\cos^2(\hat{\kappa},\hat{\kappa}')\right\}}{\kappa\kappa'(\kappa+\kappa')}$$
$$\times \left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}\right\rangle\left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}\right\rangle \quad . \tag{115}$$

The above expression may be factored by noting that the wave vector $\vec{\kappa}$ is given in the same coordinate system as the electromagnetic vector potential $\vec{A}(\vec{\rho})$. Since $\vec{R}$ is along ζ (Fig. 2), the exponential factor $\vec{\kappa}\cdot\vec{R}$ is just $\kappa R \cos(\hat{\kappa}, \hat{R})$. Additional terms depending on the angular coordinates of $\vec{\kappa}$ are contained in $\left\{1 + \cos^2(\hat{\kappa}, \hat{\kappa}')\right\}$ and the exponential factors in the matrix elements. Hence, one needs to decide on the degree of approximation to be used in the retardation factor $e^{i\vec{\kappa}\cdot\vec{r}}$ before performing the integrals over $d\Omega_{\kappa}$ and $d\Omega_{\kappa'}$. If the dipole approximation in $e^{i\vec{\kappa}\cdot\vec{r}}$ is used then the only factors depending on the angular dependence of the wave vector $\vec{\kappa}$ are the remaining two factors above. To determine the number of terms to be included in an expansion of $e^{i\vec{\kappa}\cdot\vec{r}}$, note that the coefficient of the term in equation (115) is proportional to $\left\langle r_1^2\right\rangle\left\langle r_2^2\right\rangle$. If the highest approximation is to correspond to quadrupole-quadrupole orders, then the terms proportional to $\left\langle r_1^2\right\rangle\left\langle r_2^2\right\rangle\left\langle r_1^4\right\rangle$ or $\left\langle r_1^2\right\rangle\left\langle r_2^2\right\rangle\left\langle r_2^4\right\rangle$ which correspond to dipole-octupole orders in r_2 and r_1 and to octupole-diple orders in r_2 and r_1 must be included. Hence, one needs to retain the first five terms in a power series expansion of $e^{i\vec{\kappa}\cdot\vec{r}}$; that is,

$$e^{i\vec{\kappa}\cdot\vec{r}} \cong \left\{1 + i\vec{\kappa}\cdot\vec{r} + \frac{i^2}{2}(\vec{\kappa}\cdot\vec{r})^2 + \frac{i^3}{6}(\vec{\kappa}\cdot\vec{r})^3 + \frac{i^4}{24}(\vec{\kappa}\cdot\vec{r})^4\right\} . \qquad (116)$$

Letting $(\vec{\kappa}+\vec{\kappa}') \equiv \vec{\omega}$ and using the above expansion, the matrix products of equation (115) give

$$\begin{aligned}\left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}\right\rangle\left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}\right\rangle = &\left\langle\left\{1 + i(\vec{\omega}\cdot\vec{r}_1) - \frac{1}{2}(\vec{\omega}\cdot\vec{r}_1)^2 - \frac{i}{6}(\vec{\omega}\cdot\vec{r}_1)^3 \right.\right. \\ &\left.\left. + \frac{1}{24}(\vec{\omega}\cdot\vec{r}_1)^4\right\}\right\rangle \\ &\times\left\langle\left\{1 - i(\vec{\omega}\cdot\vec{r}_2) - \frac{1}{2}(\vec{\omega}\cdot\vec{r}_2)^2 + \frac{1}{6}(\vec{\omega}\cdot\vec{r}_2)^3 \right.\right. \\ &\left.\left. + \frac{1}{24}(\vec{\omega}\cdot\vec{r}_2)^4\right\}\right\rangle .\end{aligned} \qquad (117)$$

Neglecting combined powers of r greater than the fourth power in r_1 and r_2, the above becomes

$$\left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}\right\rangle\left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}\right\rangle$$

$$= \left\langle 1\right\rangle\left\langle\left\{1 - i\,(\vec{\omega}\cdot\vec{r}_2) - \frac{1}{2}\,(\vec{\omega}\cdot\vec{r}_2)^2 + \frac{i}{6}\,(\vec{\omega}\cdot\vec{r}_2)^3 + \frac{1}{24}\,(\vec{\omega}\cdot\vec{r}_2)^4\right\}\right\rangle$$

$$+ i\left\langle\vec{\omega}\cdot\vec{r}_1\right\rangle\left\langle\left\{1 - i\,(\vec{\omega}\cdot\vec{r}_2) - \frac{1}{2}\,(\vec{\omega}\cdot\vec{r}_2)^2 + \frac{i}{6}\,(\vec{\omega}\cdot\vec{r}_2)^3\right\}\right\rangle$$

$$- \frac{1}{2}\left\langle(\vec{\omega}\cdot r_1)^2\right\rangle\left\langle\left\{1 - i\,(\vec{\omega}\cdot\vec{r}_2) - \frac{1}{2}\,(\vec{\omega}\cdot\vec{r}_2)^2\right\}\right\rangle$$

$$- \frac{i}{6}\left\langle(\vec{\omega}\cdot\vec{r}_1)^3\right\rangle\left\langle\left\{1 - i\,(\vec{\omega}\cdot\vec{r}_2)\right\}\right\rangle$$

$$+ \frac{1}{24}\left\langle(\vec{\omega}\cdot\vec{r}_1)^4\right\rangle\left\langle\left\{1\right\}\right\rangle \quad . \tag{118}$$

These matrix products simplify considerably since

$$\left\langle\vec{\omega}\cdot\vec{r}_1\right\rangle = \sum_i \omega_i\left\langle(\vec{r}_1)_i\right\rangle = 0 \;;$$

$$\left\langle(\vec{\omega}\cdot\vec{r}_1)^3\right\rangle = \sum_{i,j,\kappa} \omega_i\,\omega_j\,\omega_\kappa\left\langle(\vec{r}_1)_i(\vec{r}_1)_j(\vec{r}_1)_\kappa\right\rangle = 0 \quad ,$$

where $(\vec{r}_1)_i$ are the Cartesian components of the position vector $\vec{r}_1$. The first term is readily shown to be zero using the definitions of $(\vec{r}_1)_i$ in spherical coordinates; $\left\langle(\vec{\omega}\cdot\vec{r}_1)^3\right\rangle$ is shown to be zero since

$$\left\langle(\vec{r})_i(\vec{r})_j(\vec{r})_\kappa\right\rangle = \left\langle(\vec{r})_j(\vec{r})_\kappa(\vec{r})_i\right\rangle = \left\langle(\vec{r})_\kappa(\vec{r})_i(\vec{r})_j\right\rangle \quad .$$

In addition, all the various combinations of the $(\vec{r})_i$ components are expressed in terms of Spherical Harmonics[5] which are then integrated as sets of three products each. Incorporating these results, the nonzero terms of equation (118) are given by

$$\left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}\right\rangle\left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2}\right\rangle$$

$$= \Bigg\{ 1 - \frac{1}{2}\sum_{ts}\omega_t\,\omega_s\left[\left\langle(\vec{r}_1)_t(\vec{r}_1)_s\right\rangle + \left\langle(\vec{r}_2)_t(\vec{r}_2)_s\right\rangle\right]$$

$$+ \frac{1}{4}\sum_{ts}\sum_{qh}\omega_t\,\omega_s\,\omega_q\,\omega_h\left\langle(\vec{r}_1)_t(\vec{r}_1)_s\right\rangle\left\langle(\vec{r}_2)_q(\vec{r}_2)_h\right\rangle$$

$$+ \frac{1}{24}\sum_{ts}\sum_{qh}\omega_t\,\omega_s\,\omega_q\,\omega_h\Big[\left\langle(\vec{r}_1)_t(\vec{r}_1)_s(\vec{r}_1)_q(\vec{r}_1)_h\right\rangle$$

$$+ \left\langle(\vec{r}_2)_t(\vec{r}_2)_s(\vec{r}_2)_q(\vec{r}_2)_h\right\rangle\Big]\Bigg\} \quad . \qquad (119)$$

The above sums are evaluated using the results below, obtained for the matrix elements over $(\vec{r}_1)_i$ components.[6]

---

5. $(\vec{r}_1)_1 = -\sqrt{\frac{2\pi}{3}}\, r_1\left(Y_1^{+1} - Y_1^{-1}\right)$, $(\vec{r}_1)_2 = i\sqrt{\frac{2\pi}{3}}\, r_1\left(Y_1^{+1} + Y_1^{-1}\right)$,

   $(\vec{r}_1)_3 = \sqrt{\frac{4\pi}{3}}\, r_1\, Y_1^0$

6. The terms $\left\langle(\vec{r})_i(\vec{r})_j(\vec{r})_\kappa(\vec{r})_\ell\right\rangle$ are evaluated using the Spherical Harmonic Addition Theorem twice on each set of two, and using the fact that $\left\langle(\vec{r})_t(\vec{r})_s(\vec{r})_q(\vec{r})_h\right\rangle = \left\langle(\vec{r})_s(\vec{r})_q(\vec{r})_h(\vec{r})_t\right\rangle = \left\langle(\vec{r})_h(\vec{r})_t(\vec{r})_s(\vec{r})_q\right\rangle$.

$$\left\langle(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle = \frac{1}{3}\left\langle r_1^2\right\rangle \delta_{ij} = \left\langle R_{1,0}\right| \left\langle Y_0^0\right| \; (\vec{r}_1)_i(\vec{r}_1)_j \; \left|R_{1,0}\right\rangle \left|Y_0^0\right\rangle,$$

$$\left\langle(\vec{r}_1)_i(\vec{r}_1)_j(\vec{r}_1)_\ell(\vec{r}_1)_\kappa\right\rangle = \left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\left\langle r^4\right\rangle\left(\delta_{ij}\,\delta_{\ell\kappa} + \delta_{ij}\,\delta_{j\kappa} + \delta_{i\kappa}\,\delta_{j\ell}\right) \quad ,$$

$$\left\langle(\vec{r}_1)_i(\vec{r}_1)_j(\vec{r}_1)_\ell(\vec{r}_1)_\kappa\right\rangle = \left(\frac{1}{5}\right)\left\langle r_1^4\right\rangle \delta_{ij}\,\delta_{j\ell}\,\delta_{\ell\kappa} \quad , \tag{120}$$

where $\langle r^2 \rangle$ and $\langle r^4 \rangle$ are matrix elements taken over the radial portion of the atomic eigenstates given by equation (86). To obtain results in terms of κ and κ' and their corresponding angular coordinates, one replaces $\vec{\omega}$ by $(\vec{\kappa}+\vec{\kappa}')$ at the end of each calculation. For instance, the second term of equation (119) may be expanded using the results of equation (120) in which case one gets

$$\sum_{ts} \omega_t\,\omega_s \left\langle(\vec{r}_1)_t(\vec{r}_1)_s\right\rangle = \frac{1}{3}\left\langle r_1^2\right\rangle \sum_{t,s} \omega_t\,\omega_s\,\delta_{ts}$$

$$= \frac{1}{3}\left\langle r_1^2\right\rangle\left[\kappa^2 + \kappa'^2 + 2\kappa\kappa' \cos(\hat{\kappa},\hat{\kappa}')\right] \quad . \tag{121}$$

Following the same procedure, the terms of equation (119) are expressed in terms of κ, κ' and $\cos(\hat{\kappa},\hat{\kappa}')$. Substituting these results in equation (115), one obtains

$$\begin{aligned} X(1) = {} & \left(-\frac{2\hbar}{2^5\pi^4\mu^2c^3}\right) \int_0^\infty \kappa^2 d\kappa \int_{4\pi} d\Omega_\kappa \int_0^\infty \kappa'^2 d\kappa' \int_{4\pi} d\Omega_{\kappa'} \frac{\left\{1 + \cos^2(\hat{\kappa},\hat{\kappa}')\right\} e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{\kappa\kappa'(\kappa+\kappa')} \\ & \times\Bigg\{1 - \frac{1}{2}\left(\frac{1}{3}\right)\left[\left\langle r_1^2\right\rangle + \left\langle r_2^2\right\rangle\right]\left[(\kappa^2+\kappa'^2) + 2\kappa\kappa'\cos(\hat{\kappa},\hat{\kappa}')\right] \\ & + \left(\frac{1}{4}\right)\left[\left(\frac{1}{3}\right)^2 \left\langle r_1^2\right\rangle\left\langle r_2^2\right\rangle + \left(\frac{1}{6}\right)\left(\frac{1}{5}\right)\left(\left\langle r_1^4\right\rangle + \left\langle r_2^4\right\rangle\right)\right] \\ & \times\left[(\kappa^2+\kappa'^2)^2 + 4\kappa\kappa'(\kappa^2+\kappa'^2)\cos(\hat{\kappa},\hat{\kappa}') + 4\kappa^2\kappa'^2\cos^2(\hat{\kappa},\hat{\kappa}')\right]\Bigg\} \quad . \end{aligned} \tag{122}$$

Defining $\cos(\hat{\kappa}, \hat{\kappa}') \equiv \cos\Theta$, equation (122) may be written as

$$X(1) = \left(-\frac{2\hbar}{2^5 \pi^4 \mu^2 c^3}\right) \int_0^\infty \kappa^2 d\kappa \int_0^\infty \kappa'^2 d\kappa' \left[\frac{1}{\kappa\kappa' (\kappa + \kappa')}\right] \int d\Omega_\kappa \int d\Omega_{\kappa'}\, e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}$$

$$\times \left\{ (1 + \cos^2\Theta) - \frac{1}{2}\left(\frac{1}{3}\right)\left(\langle r_1^2\rangle + \langle r_2^2\rangle\right)\left[(\kappa^2 + \kappa'^2)(1 + \cos^2\Theta) + 2\kappa\kappa' (\cos\Theta + \cos^3\Theta)\right]\right.$$

$$+ \frac{1}{4}\left[\left(\frac{1}{3}\right)\langle r_1^2\rangle\langle r_2^2\rangle + \left(\frac{1}{6}\right)\left(\frac{1}{5}\right)\left(\langle r_1^4\rangle + \langle r_2^4\rangle\right)\right]$$

$$\left.\times \left[(\kappa^2 + \kappa'^2)(1 + \cos^2\Theta) + 4\kappa\kappa' (\kappa^2 + \kappa'^2)(\cos\Theta + \cos^3\Theta) + 4\kappa^2\kappa'^2 (\cos^2\Theta + \cos^4\Theta)\right]\right\} \quad . \qquad (123)$$

In the above result, the various approximations are separated as follows: the first factor, containing only $(1 + \cos^2\Theta)$, corresponds to the dipole-dipole approximation; the second term containing a more complex dependence on Θ, corresponds to the dipole-quadrupole approximation; and the last term corresponds to the quadrupole-quadrupole approximation. In subsequent calculations the various $X(i)$ terms will be put in this format.

The next term to be considered is $X(2)$, defined by equation (106). $X(2)$ may be recombined by interchanging the coordinates of atoms I and II in the second, fourth, and fifth terms; this results in the following expression:

$$X(2) = \left[\frac{2(E_1 - E_0)^2}{2^4 \pi^4 \mu c^3 \hbar}\right] \int \frac{d\vec{\kappa}}{\kappa} \int \frac{d\vec{\kappa}'}{\kappa'} \sum_{ij} \left\{\delta_{ij} - (\hat{\kappa})_i(\hat{\kappa})_j - (\hat{\kappa}')_i(\hat{\kappa}')_j + (\hat{\kappa})_i(\hat{\kappa}')_j(\hat{\kappa}\cdot\hat{\kappa}')\right\}$$

$$\times \left\{ \frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa + \kappa')\left[(E_1 - E_0) + \hbar c\kappa\right]} \left\langle e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}\right\rangle \left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_i (\vec{r}_2)_j\right\rangle \right.$$

$$+ \frac{\hbar c\, e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c\kappa\right]\left[(E_1 - E_0) + \hbar c\kappa'\right]} \left\langle e^{+i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_1}\right\rangle \left\langle e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_i (\vec{r}_2)_j\right\rangle$$

$$\left. + \frac{e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa + \kappa')\left[(E_1 - E_0) + \hbar c\kappa'\right]} \left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1}\right\rangle \left\langle e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_i (\vec{r}_2)_j\right\rangle \right\} \quad . \qquad (124)$$

Noting that the coefficient of the above expression is proportional to $\langle r_1^2\rangle$, and that the factors $(\vec{r}_2)_i (\vec{r}_2)_j$ in the above matrix elements give results proportional to $\langle r_2^2 \rangle$,[7] one needs to retain the first five terms in the expansion for $e^{i\vec{\kappa}\cdot\vec{r}}$ in order to obtain results accurate to quadrupole-quadrupole orders. To simplify this expression, one needs to show that the expansions due to $e^{i\vec{\kappa}\cdot\vec{r}}$ for each of the terms in equation (124) yield similar results. The matrix product (letting $\vec{\omega} = \vec{\kappa}+\vec{\kappa}'$) corresponding to the first term in equation (124) is given by

$$\left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1} \right\rangle \left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle$$

$$= \Bigg[\left\langle \left\{ 1 + i(\vec{\omega}\cdot\vec{r}_1) - \frac{1}{2}(\vec{\omega}\cdot\vec{r}_1)^2 - \frac{i}{6}(\vec{\omega}\cdot\vec{r}_1)^3 + \frac{1}{24}(\vec{\omega}\cdot\vec{r}_1)^4 \right\} \right\rangle \left\langle (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle$$

$$+ \left\langle \left\{ 1 + i(\vec{\omega}\cdot\vec{r}_1) - \frac{1}{2}(\vec{\omega}\cdot\vec{r}_1)^2 - \frac{i}{6}(\vec{\omega}\cdot\vec{r}_1)^3 + \frac{1}{24}(\vec{\omega}\cdot\vec{r}_1)^4 \right\} \right\rangle \left\langle -i(\vec{\omega}\cdot\vec{r}_2)(\vec{r}_2)_i (\vec{r}_2)_j \right\rangle$$

$$+ \left\langle \left\{ 1 + i(\vec{\omega}\cdot\vec{r}_1) - \frac{1}{2}(\vec{\omega}\cdot\vec{r}_1)^2 - \frac{i}{6}(\vec{\omega}\cdot\vec{r}_1)^3 + \frac{1}{24}(\vec{\omega}\cdot\vec{r}_1)^4 \right\} \right\rangle \left\langle -\frac{1}{2}(\vec{\omega}\cdot\vec{r}_2)^2(\vec{r}_2)_i (\vec{r}_2)_j \right\rangle$$

$$+ \left\langle \left\{ 1 + i(\vec{\omega}\cdot\vec{r}_1) - \frac{1}{2}(\vec{\omega}\cdot\vec{r}_1)^2 - \frac{i}{6}(\vec{\omega}\cdot\vec{r}_1)^3 + \frac{1}{24}(\vec{\omega}\cdot\vec{r}_1)^4 \right\} \right\rangle \left\langle +\frac{i}{6}(\vec{\omega}\cdot\vec{r}_2)^3(\vec{r}_2)_i (\vec{r}_2)_j \right\rangle$$

$$+ \left\langle \left\{ 1 + i(\vec{\omega}\cdot\vec{r}_1) - \frac{1}{2}(\vec{\omega}\cdot\vec{r}_1)^2 - \frac{i}{6}(\vec{\omega}\cdot\vec{r}_1)^3 + \frac{1}{24}(\vec{\omega}\cdot\vec{r}_1)^4 \right\} \right\rangle \left\langle \frac{1}{24}(\vec{\omega}\cdot\vec{r}_2)^4(\vec{r}_2)_j (\vec{r}_2)_j \right\rangle \Bigg] .$$

Retaining only the appropriate terms and neglecting the terms proportional to $\langle (\vec{r})_i \rangle$ and $\langle (\vec{r})_i (\vec{r})_j (\vec{r})_\ell \rangle$, one gets

$$\left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1} \right\rangle \left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle = \Bigg[\left\{ \langle 1 \rangle - \frac{1}{2}\left\langle (\vec{\omega}\cdot\vec{r}_1)^2 \right\rangle + \frac{1}{24}\left\langle (\vec{\omega}\cdot\vec{r}_1)^4 \right\rangle \right\} \left\langle (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle$$
$$+ \left\{ \langle 1 \rangle - \frac{1}{2}\left\langle (\vec{\omega}\cdot\vec{r}_1)^2 \right\rangle \right\} \left\langle -\frac{1}{2}(\vec{\omega}\cdot\vec{r}_2)^2 (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle$$
$$+ \left\{ \langle 1 \rangle \right\} \left\langle +\frac{i}{6}(\vec{\omega}\cdot\vec{r}_2)^3 (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle \qquad (125)$$
$$+ \left\{ \langle 1 \rangle \right\} \left\langle \frac{1}{24}(\vec{\omega}\cdot\vec{r}_2)^4 (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle \Bigg] .$$

---

7. These factors alone, when $e^{i\vec{\kappa}\cdot\vec{r}} \rightarrow 1$, give the dipole-dipole approximation.

All but the last two factors in equation (125) have been evaluated previously. The remaining terms are evaluated as follows. Take $\left\langle \frac{i}{6} (\vec{\omega}\cdot\vec{r}_2)^3 (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle$; this term is proportional to $\left\langle (\vec{r}_2)_i (\vec{r}_2)_j (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_q \right\rangle$, where i, j, t, s, and q run over 1, 2, 3, corresponding to the x, y, z components of $\vec{r}$. Expressing the above factors in terms of Spherical Harmonics and using the Spherical Harmonic Addition Theorem on each set, one shows that all the above terms vanish. Incorporating these results in equation (125) yields

$$\left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1)} \right\rangle \left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle$$

$$= \left\{ \left\langle 1 \right\rangle \left\langle (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle - \frac{1}{2} \left\langle (\vec{\omega}\cdot\vec{r}_1)^2 \right\rangle \left\langle (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle - \frac{1}{2} \left\langle (\vec{\omega}\cdot\vec{r}_2)^2 (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle \right.$$

$$+ \frac{1}{24} \left\langle (\vec{\omega}\cdot\vec{r}_1)^4 \right\rangle \left\langle (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle + \frac{1}{4} \left\langle (\vec{\omega}\cdot\vec{r}_1)^2 \right\rangle \left\langle (\vec{\omega}\cdot\vec{r}_2)^2 (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle$$

$$\left. + \frac{1}{24} \left\langle (\vec{\omega}\cdot\vec{r}_2)^4 (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle \right\} . \tag{126}$$

Letting $(\vec{\kappa}-\vec{\kappa}') \equiv \vec{v}$, one obtains a similar expression as given above for the matrix products of the second term in equation (124). The last term in equation (124) gives the same results as given by equation (126). This is because of the alternation of plus and minus signs in the various products in equation (125). The terms having opposite signs are those which do not contribute. By combining the first and last terms in equation (124), X(2) becomes

$$
\begin{aligned}
X(2) = & \left[\frac{2(E_1 - E_0)^2}{2^4 \pi^4 \mu c^3 \hbar}\right] \int \frac{d\vec{\kappa}}{\kappa} \int \frac{d\vec{\kappa}'}{\kappa'} \sum_{ij} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j - (\hat{\kappa}')_i (\hat{\kappa}')_j + (\hat{\kappa})_i (\hat{\kappa}')_j (\hat{\kappa}\cdot\hat{\kappa}') \right\} \\
& \times \Bigg\{ \left[\frac{e^{-(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa+\kappa')\left[(E_1 - E_0) + \hbar c \kappa\right]} + \frac{e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa+\kappa')\left[(E_1 - E_0) + \hbar c \kappa'\right]} \right] \\
& \times \Bigg[\left(\frac{1}{3}\right) \langle r_2^2 \rangle \delta_{ij} - \frac{1}{2} \sum_{ts} \left\{ \left(\frac{1}{3}\right)^2 \langle r_1^2 \rangle \langle r_2^2 \rangle \omega_t \omega_s \delta_{ts} \delta_{ij} + \omega_t \omega_s \left\langle (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle \right\} \\
& + \frac{1}{4} \sum_{ts} \sum_{qh} \Bigg\{ \left(\frac{1}{6}\right)\left(\frac{1}{3}\right) \langle r_2^2 \rangle \delta_{ij} \omega_t \omega_s \omega_q \omega_h \left\langle (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_q (\vec{r}_1)_h \right\rangle \\
& \qquad + \left(\frac{1}{3}\right) \langle r_1^2 \rangle \omega_t \omega_s \delta_{ts} \omega_q \omega_h \left\langle (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle \\
& \qquad + \left(\frac{1}{6}\right) \omega_t \omega_s \omega_q \omega_h \left\langle (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle \Bigg\} \Bigg] \\
& + \left[\frac{\hbar c\, e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c \kappa\right]\left[(E_1 - E_0) + \hbar c \kappa'\right]} \right] \\
& \times \Bigg[\left(\frac{1}{3}\right) \langle r_2^2 \rangle \delta_{ij} - \frac{1}{2} \sum_{ts} \left\{ \left(\frac{1}{3}\right)^2 \langle r_1^2 \rangle \langle r_2^2 \rangle v_t v_s \delta_{ts} \delta_{ij} + v_t v_s \left\langle (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle \right\} \\
& + \frac{1}{4} \sum_{ts} \sum_{qh} \Bigg\{ \left(\frac{1}{6}\right)\left(\frac{1}{3}\right) \langle r_2^2 \rangle \delta_{ij} v_t v_s v_q v_h \left\langle (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_q (\vec{r}_1)_h \right\rangle \\
& \qquad + \left(\frac{1}{3}\right) \langle r_1^2 \rangle v_t v_s \delta_{ts} v_q v_h \left\langle (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle \\
& \qquad + \left(\frac{1}{6}\right) v_t v_s v_q v_h \left\langle (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle \Bigg\} \Bigg] \Bigg\} .
\end{aligned}
\tag{127}
$$

The above expression may be simplified further; but for the present purposes, this is adequate since at this point one wishes only to separate the various terms corresponding to the various approximations.[8]

The next term to be evaluated is $X(3)$, defined by equation (109). This expression may be recombined using the following procedure. Interchange coordinates of atoms I and II in every other term in equation (109) and rearrange the quantities within the matrix elements, remembering that the order of the terms does not matter. After expanding exponentials, one obtains

---

8. Note that the sums over i, j are more complex and that one needs to calculate $\left\langle (\vec{r}_2)_i (\vec{r}_2)_j (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_q (\vec{r}_2)_h \right\rangle$.

$$
\begin{aligned}
X(3) = & \left[-\frac{4(E_1 - E_0)^2}{2^3 \pi^2 \hbar c} \right] \int \frac{d\vec{\kappa}}{\kappa} \sum_{ij} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j \right\} e^{-i\vec{\kappa}\cdot\vec{R}} \\
& \times \left\{ \frac{1}{(E_1 - E_0)\left[(E_1 - E_0) + \hbar c\kappa\right]} + \frac{-1}{\left[(E_1 - E_0) + \hbar c\kappa\right]\left[(E_1 - E_0) + \hbar c\kappa\right]} \right\} \\
& \times \left\{ \left\langle H_q^{(2)} (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle + i \sum_t \kappa_t \left[\left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle - \left\langle H_q^{(2)} (\vec{r}_1)_i (\vec{r}_2)_t (\vec{r}_2)_j \right\rangle \right] \right. \\
& - \frac{1}{2} \sum_{ts} \kappa_t \kappa_s \left[\left\langle H_q^{(2)} (\vec{r}_1)_i (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_j \right\rangle - 2 \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_i (\vec{r}_2)_s (\vec{r}_2)_j \right\rangle \right. \\
& \qquad \left. + \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle \right] \\
& + \frac{i}{6} \sum_t \sum_s \sum_l \kappa_t \kappa_s \kappa_l \left[\left\langle H_q^{(2)} (\vec{r}_1)_i (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_l (\vec{r}_2)_j \right\rangle - 3 \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_i (\vec{r}_2)_s (\vec{r}_2)_l (\vec{r}_2)_j \right\rangle \right. \\
& \qquad \left. + 3 \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_i (\vec{r}_2)_l (\vec{r}_2)_j \right\rangle - \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_l (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle \right] \\
& + \frac{1}{24} \sum_{ts} \sum_{lh} \kappa_t \kappa_s \kappa_l \kappa_h \\
& \times \left[\left\langle H_q^{(2)} (\vec{r}_1)_i (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_l (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle - 4 \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_i (\vec{r}_2)_s (\vec{r}_2)_l (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle \right. \\
& + 6 \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_i (\vec{r}_2)_l (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle - 4 \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_l (\vec{r}_1)_i (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle \\
& \left. \left. + \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_l (\vec{r}_1)_h (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle \right] \right\} . \qquad (128)
\end{aligned}
$$

$X(3)$ is obtained by expanding both exponentials in $\vec{\kappa}\cdot\vec{r}_1$ and $\vec{\kappa}\cdot\vec{r}_2$ and neglecting the matrix terms proportional to the power of r greater than six. Neglecting the higher powers is necessary since if one sets exponentials equal to unity, the leading term is $\left\langle H_q^{(2)} (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle$. The lowest term in $H_q^{(2)}$ corresponds to terms proportional to $(\vec{r}_1)^1 (\vec{r}_2)^1$ which makes the last terms in equation (128) proportional to $\langle r_1^6 \, r_2^2 \rangle$. These factors then correspond to the desired octupole-dipole orders. The above results are further simplified by making use of the r_1, r_2 dependence of $H_q^{(2)}$. For instance, the sum

$\sum_{ij} (\;) \sum_t \kappa_t \left\{ \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle - \left\langle H_q^{(2)} (\vec{r}_2)_i (\vec{r}_2)_t (\vec{r}_2)_j \right\rangle \right\}$ adds up to zero, even though each individual term does not necessarily vanish. For example, in evaluating the term $\left\langle H_q^{(2)} \; (\vec{r}_1)_2 (\vec{r}_1)_2 (\vec{r}_2)_3 \right\rangle$, one replaces the components $(\vec{r}_1)_i$ by their respective Spherical Harmonic equivalents, and then substitutes for $H_q^{(2)}$ in terms of $r_1^{L_1}$ and $r_2^{L_2}$, and $Y_{L_1}^{M*}$ and $Y_{L_2}^{-M*}$. Factoring the matrix elements into factors depending only on atoms I or II, one finds that the conditions for nonzero terms resulting from the Spherical Harmonics require the sums over L_1 and L_2 to terminate at a given L_1, L_2 value. Hence, choosing the lowest L, one sums over the appropriate range over M. In this case the term gives a nonzero result which in turn is cancelled by $\left\langle H_q^{(2)} \; (\vec{r}_1)_3 (\vec{r}_2)_2 (\vec{r}_2)_2 \right\rangle$. A similar procedure is used to show that the fourth factor in equation (128), consisting of four terms of the form $\left\langle H_q^{(2)} \; (\vec{r}_2)_q (\vec{r}_1)_i (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_j \right\rangle$, adds up to zero. This may be verified quickly by taking each corresponding set of terms and interchanging the labels on the quantities, and, since $H_q^{(2)} \; (r_1, r_2) = H_q^{(2)} \; (r_2, r_1)$, the sum of terms vanishes identically. Thus, the nonzero terms which contribute to equation (128) are given by

$$
\begin{aligned}
X(3) = & \left[- \frac{4 (E_1 - E_0)^2}{2^3 \pi^2 \hbar c} \right] \int_0^\infty \kappa \, d\kappa \int d\Omega_\kappa \sum_{ij} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j \right\} e^{-i \vec{\kappa} \cdot \vec{R}} \\
& \times \left\{ \frac{1}{(E_1 - E_0) \left[(E_1 - E_0) + \hbar c \kappa \right]} + \frac{-1}{\left[(E_1 - E_0) + \hbar c \kappa \right] \left[(E_1 - E_0) + \hbar c \kappa \right]} \right\} \\
& \times \Bigg\{ \left\langle H_q^{(2)} \; (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle - \frac{1}{2} \sum_{ts} \kappa_t \kappa_s \Big[\left\langle H_q^{(2)} \; (\vec{r}_1)_i (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_j \right\rangle - 2 \left\langle H_q^{(2)} \; (\vec{r}_1)_t (\vec{r}_1)_i (\vec{r}_2)_s (\vec{r}_2)_j \right\rangle \\
& \qquad + \left\langle H_q^{(2)} \; (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle \Big] \\
& + \frac{1}{24} \sum_{ts} \sum_{lh} \kappa_t \kappa_s \kappa_l \kappa_h \\
& \times \Big[\left\langle H_q^{(2)} \; (\vec{r}_1)_i (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_l (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle - 4 \left\langle H_q^{(2)} \; (\vec{r}_1)_t (\vec{r}_1)_i (\vec{r}_2)_s (\vec{r}_2)_l (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle \\
& + 6 \left\langle H_q^{(2)} \; (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_i (\vec{r}_2)_l (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle - 4 \left\langle H_q^{(2)} \; (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_l (\vec{r}_1)_i (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle \\
& + \left\langle H_q^{(2)} \; (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_l (\vec{r}_1)_h (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle \Big] \Bigg\} .
\end{aligned}
\tag{129}
$$

Later on, subsequent simplifications will be performed when each of the preceding terms is considered.

The next group of terms to be considered is defined by X(4) and is given in equation (113). X(4) is simplified using the same techniques as before and results in the following expression:

$$
\begin{aligned}
X(4) = & \left[-\frac{2(E_1 - E_0)^4}{2^4 \pi^4 \hbar^2 c^2} \right] \int \frac{d\vec{\kappa}}{\kappa} \int \frac{d\vec{\kappa}'}{\kappa'} \sum_{ij} \sum_{\ell s} \left\{ \delta_{is} - (\hat{\kappa})_i (\hat{\kappa})_s \right\} \left\{ \delta_{j\ell} - (\hat{\kappa}')_j (\hat{\kappa}')_\ell \right\} \\
& \times \left[\left\{ \frac{1}{\left[(E_1 - E_0) + \hbar c \kappa\right]\left[\hbar c \kappa + \hbar c \kappa'\right]\left[(E_1 - E_0) + \hbar c \kappa\right]} \right. \right. \\
& + \frac{1}{\left[(E_1 - E_0) + \hbar c \kappa\right]\left[\hbar c \kappa + \hbar c \kappa'\right]\left[(E_1 - E_0) + \hbar c \kappa'\right]} \\
& \left. + \frac{1}{\left[(E_1 - E_0) + \hbar c \kappa\right]\left[(E_1 - E_0) + (E_1 - E_0)\right]\left[(E_1 - E_0) + \hbar c \kappa'\right]} \right\} \\
& \times e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \left\langle e^{i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_1} (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \\
& + \left\{ \frac{1}{\left[(E_1 - E_0) + \hbar c \kappa\right]\left[(E_1 - E_0) + (E_1 - E_0) + \hbar c \kappa + \hbar c \kappa'\right]\left[(E_1 - E_0) + \hbar c \kappa\right]} \right. \\
& + \frac{1}{\left[(E_1 - E_0) + \hbar c \kappa\right]\left[(E_1 - E_0) + (E_1 - E_0) + \hbar c \kappa + \hbar c \kappa'\right]\left[(E_1 - E_0) + \hbar c \kappa'\right]} \\
& \left. + \frac{1}{\left[(E_1 - E_0) + \hbar c \kappa\right]\left[(E_1 - E_0) + (E_1 - E_0)\right]\left[(E_1 - E_0) + \hbar c \kappa'\right]} \right\} \\
& \left. \times e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}} \left\langle e^{i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_1} (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}_2} (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \right] . \qquad (130)
\end{aligned}
$$

Expanding the exponentials as before and retaining the appropriate terms, we now have

$$
\begin{aligned}
X(4) = {} & \left[- \frac{2(E_1 - E_0)^4}{2^4 \pi^4 \hbar^2 c^2} \right] \int \kappa \, d\kappa \int \kappa' \, d\kappa' \int d\Omega_\kappa \int d\Omega_{\kappa'} \times \sum_{ij} \sum_{\ell s} \left\{ \delta_{is} - (\hat{\kappa})_i (\hat{\kappa})_s \right\} \left\{ \delta_{j\ell} - (\hat{\kappa}')_j (\hat{\kappa}')_\ell \right\} \\
& \times \Bigg[\frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{\hbar c(\kappa + \kappa')} \left\{ \frac{1}{\left[(E_1 - E_0) + \hbar c\kappa\right]^2} + \frac{1}{\left[(E_1 - E_0) + \hbar c\kappa\right]\left[(E_1 - E_0) + \hbar c\kappa'\right]} \left[1 + \frac{\hbar c(\kappa + \kappa')}{2(E_1 - E_0)} \right] \right\} \\
& \times \Bigg\{ \left(\frac{1}{3}\right) \langle r_1^2 \rangle \left(\frac{1}{3}\right) \langle r_2^2 \rangle \delta_{ij} \delta_{\ell s} - \frac{1}{2} \sum_{tq} \omega_t \omega_q \Big[\left\langle (\vec{r}_1)_t (\vec{r}_1)_q (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \\
& \qquad + \left\langle (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_t (\vec{r}_2)_q (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \Big] \\
& + \frac{1}{24} \sum_{tq} \sum_{hf} \omega_t \omega_q \omega_h \omega_f \times \Big[\left\langle (\vec{r}_1)_t (\vec{r}_1)_q (\vec{r}_1)_h (\vec{r}_1)_f (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \\
& \qquad + 6 \left\langle (\vec{r}_1)_t (\vec{r}_1)_q (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_h (\vec{r}_2)_f (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \\
& \qquad + \left\langle (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_t (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_f (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \Big] \Bigg\} \\
& + \frac{e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c\kappa\right]} \left\{ \frac{1}{2(E_1 - E_0)\left[(E_1 - E_0) + \hbar c\kappa'\right]} \right. \\
& \qquad \left. + \frac{1}{\left[2(E_1 - E_0) + \hbar c\kappa + \hbar c\kappa'\right]} \left[\frac{1}{(E_1 - E_0) + \hbar c\kappa} + \frac{1}{(E_1 - E_0) + \hbar c\kappa'} \right] \right\} \\
& \times \Bigg\{ \left(\frac{1}{3}\right) \langle r_1^2 \rangle \left(\frac{1}{3}\right) \langle r_2^2 \rangle \delta_{ij} \delta_{\ell s} - \frac{1}{2} \sum_{tq} v_t v_q \Big[\left\langle (\vec{r}_1)_t (\vec{r}_1)_q (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \\
& \qquad + \left\langle (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_t (\vec{r}_2)_q (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \Big] \\
& + \frac{1}{24} \sum_{tq} \sum_{hf} v_t v_q v_h v_f \times \Big[\left\langle (\vec{r}_1)_t (\vec{r}_1)_q (\vec{r}_1)_h (\vec{r}_1)_f (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \\
& \qquad + 6 \left\langle (\vec{r}_1)_t (\vec{r}_1)_q (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_h (\vec{r}_2)_f (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \\
& \qquad + \left\langle (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_t (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_f (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \Big] \Bigg\} \Bigg] .
\end{aligned}
\tag{131}
$$

The above expression has two distinct terms with coefficients $e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{r}}$ and $e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{r}}$, as well as various denominators. Subsequent calculations show that the two terms may be combined into a simpler expression. This will not be done in general, rather each one of the above terms will be considered as corrections to various multipole orders of the electrostatic interaction energy given by equation (85). Once the X(i) terms are defined, as above, one can write the interaction energy ΔE in terms of corrections resulting from various approximations as

$$\Delta E/e^4 = \Delta E_{d-d} + \Delta E_{d-q} + \Delta E_{q-q} \quad .$$

Dipole-Approximation ΔE_{d-d}

The terms corresponding to the correction energy ΔE have been given as sums of terms corresponding to the various approximations to be considered in this calculation. To evaluate the first term ΔE_{d-d}, which belongs to the dipole-dipole approximation, one collects all the first terms in the $X(i)$ expressions and adds them to the electrostatic dipole-dipole interaction term given by equation (85). These terms are obtained by letting $L_1 = L_2 = 1$ and $m = -1, 0, +1$ in equation (85); this yields

$$\Delta E\left(H_q^{(2)}\right)_{d-d} = \sum_{m=-1}^{+1} \frac{(-1)^2 \left\{(2)!\right\}^2 \left\langle R_{1,0}(I) \left| r_1^2 \right| R_{1,0}(I)\right\rangle \left\langle R_{1,0}(II) \left| r_2^2 \right| R_{1,0}(II)\right\rangle}{2(E_0 - E_1)\, R^6 \left[(3)(3)\,(1-m)!(1+m)!(1-m)!(1+m)!\right]} \quad . \tag{132}$$

Summing over m, and redefining this quantity as $X(0)^{(1)}$, one obtains[9]

$$X(0)^{(1)} = -\frac{\langle r_1^2\rangle \langle r_2^2\rangle}{3R^6\,(E_1 - E_0)} \quad . \tag{133}$$

The corrections to this term, due to $X(i)$, where $i = 1, 2, 3, 4$, are given by the first term in each of the expressions given by equations (123), (127), (129), and (131). Combining these leading terms, the interaction energy ΔE to first order (dipole-dipole approximation) is given by

---

9. Note that $\langle r_1^2 \rangle$ is a matrix taken over only the radial portion of the eigenfunction given in equation (86).

$$
\begin{aligned}
\Delta E_{d\text{-}d} = & \left[- \frac{\langle r_1^2 \rangle \langle r_2^2 \rangle}{3R^6 (E_1 - E_0)} \right] \\
& + \left(\frac{-\hbar}{2^4 \pi^4 \mu^2 c^3} \right) \int \frac{d\vec{\kappa}}{\kappa} \int \frac{d\vec{\kappa}'}{\kappa'} \left(\frac{1}{\kappa + \kappa'} \right) e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} (1 + \cos^2 \Theta) \\
& + \left[\frac{(E_1 - E_0)^2}{2^3 \pi^4 \mu c^3 \hbar} \right] \int \frac{d\vec{\kappa}}{\kappa} \int \frac{d\vec{\kappa}'}{\kappa'} \sum_{ij} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j - (\hat{\kappa}')_i (\hat{\kappa}')_j + (\hat{\kappa})_i (\hat{\kappa}')_j (\hat{\kappa}\cdot\hat{\kappa}') \right\} \left(\frac{1}{3} \right) \langle r_2^2 \rangle \, \delta_{ij} \\
& \times \left\{ \frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa + \kappa') \left[(E_1 - E_0) + \hbar c \kappa \right]} + \frac{e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa + \kappa') \left[(E_1 - E_0) + \hbar c \kappa' \right]} + \frac{\hbar c \, e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c \kappa \right] \left[(E_1 - E_0) + \hbar c \kappa' \right]} \right\} \\
& + \left[- \frac{(E_1 - E_0)^2}{2 \pi^2 \hbar c} \right] \int \frac{d\vec{\kappa}}{\kappa} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j \right\} e^{-i\vec{\kappa}\cdot\vec{R}} \left\langle H_q^{(2)} \, (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle \\
& \qquad \times \left\{ \frac{1}{(E_1 - E_0) \left[(E_1 - E_0) + \hbar c \kappa \right]} + \frac{-1}{\left[(E_1 - E_0) + \hbar c \kappa \right] \left[(E_1 - E_0) + \hbar c \kappa \right]} \right\} \\
& + \left[- \frac{(E_1 - E_0)^4}{2^3 \pi^4 \hbar^2 c^2} \right] \int \frac{d\vec{\kappa}}{\kappa} \int \frac{d\vec{\kappa}'}{\kappa'} \sum_{ij} \sum_{\ell s} \left\{ \delta_{is} - (\hat{\kappa})_i (\hat{\kappa})_s \right\} \left\{ \delta_{j\ell} - (\hat{\kappa}')_j (\hat{\kappa}')_\ell \right\} \left\{ \left(\frac{1}{3} \right)^2 \langle r_1^2 \rangle \langle r_2^2 \rangle \, \delta_{ij} \, \delta_{\ell s} \right\} \\
& \times \left\{ \frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{\hbar c (\kappa + \kappa')} \left[\frac{1}{\left[(E_1 - E_0) + \hbar c \kappa \right]^2} + \frac{1}{\left[(E_1 - E_0) + \hbar c \kappa \right] \left[(E_1 - E_0) + \hbar c \kappa' \right]} \left\{ 1 + \frac{\hbar c (\kappa + \kappa')}{2 (E_1 - E_0)} \right\} \right] \right. \\
& \qquad + \frac{e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c \kappa \right]} \left[\frac{1}{2(E_1 - E_0) \left[(E_1 - E_0) + \hbar c \kappa' \right]} \right. \\
& \qquad \qquad \left. \left. + \frac{1}{\left[2(E_1 - E_0) + \hbar c \kappa + \hbar c \kappa' \right]} \times \left\{ \frac{1}{(E_1 - E_0) + \hbar c \kappa} + \frac{1}{(E_1 - E_0) + \hbar c \kappa'} \right\} \right] \right\}
\end{aligned}
\tag{134}
$$

This expression may be readily simplified by summing over the i, j and ℓ, s. These sums contract easily due to the δ-functions included in the respective terms. When evaluated, the sums in question give

$$\sum_{ij}\left\{\delta_{ij}-(\hat{\kappa})_i(\hat{\kappa})_j-(\hat{\kappa}')_i(\hat{\kappa}')_j+(\hat{\kappa})_i(\hat{\kappa}')_j(\hat{\kappa}\cdot\hat{\kappa}')\right\}\delta_{ij}$$

$$=\sum_{ij}\sum_{\ell s}\left\{\delta_{is}-(\hat{\kappa})_i(\hat{\kappa})_s\right\}\left\{\delta_{j\ell}-(\hat{\kappa}')_j(\hat{\kappa}')_\ell\right\}\delta_{ij}\,\delta_{\ell s}\quad,$$

$$=\left\{1+\cos^2(\hat{\kappa},\hat{\kappa}')\right\}\quad. \tag{135}$$

Further simplification is attained by expressing all the coefficients in terms of $\langle r_1^2\rangle$ and $\langle r_2^2\rangle$. This is accomplished by using the sum rule [1,19]

$$\sum_I\left(\frac{1}{2\mu c^2}\right)\delta_{ij}=\sum_m\frac{\langle\alpha|\,[P(I)]_i\,|m\rangle\langle m|\,[\vec{P}(I)]_j\,|\alpha\rangle+\langle\alpha|\,[\vec{P}(I)]_j\,|m\rangle\langle m|\,[\vec{P}(I)]_i\,|\alpha\rangle}{2\mu^2c^2\,(E_1-E_0)}\quad, \tag{136}$$

and the approximation [15] $\langle\ell\,|\,\vec{P}\,|\,m\rangle=\frac{i\mu}{\hbar}\left(E_\ell-E_m\right)\langle\ell\,|\,\vec{r}\,|\,m\rangle$, given in equation (98).[10] The sum over I is over the electrons of atom I and the sum over m is over the 2p atomic states. Hence, the quantity $1/2\mu c^2$ is replaced by $\dfrac{\langle r^2\rangle(E_1-E_0)}{3(\hbar c)^2}$, which is obtained by carrying out the indicated operations above. Using the results obtained in Appendix B for the integral over solid angles $d\Omega_\kappa$ and $d\Omega_{\kappa'}$ and using the definitions $\kappa R\equiv b$, $\kappa' R\equiv\beta$, the second term in equation (134) reduces to

$$X(1)^{(1)}=-\frac{2^3\hbar c\,(E_1-E_0)^2\langle r_1^2\rangle\langle r_2^2\rangle}{3^2\pi^2(\hbar c)^4R^3}\int_0^\infty b\,db\int_0^\infty\frac{\beta\,d\beta\,\{F(b)\,F(\beta)+2G(b)\,G(\beta)\}}{(b+\beta)}\quad, \tag{137}$$

10. Reference 19 gives this as $4\pi\mu\sum_{\alpha'}\nu(\alpha',\alpha)\;|\langle\alpha\,|\,\vec{r}\,|\,\alpha'\rangle|^2=3\hbar$, where $(E_{\alpha'}-E_\alpha)=2\pi\hbar\nu(\alpha',\alpha)$.

where

$$F(b) = \left[\frac{\sin b}{b} + G(b)\right] , \quad G(b) = \left(\frac{\cos b}{b^2} - \frac{\sin b}{b^3}\right) ,$$

where one defines the above expression as in $X(0)^{(1)}$, the superscript denotes the degree of approximation as before. Letting $(E_1 - E_0)R/\hbar c = a$, the coefficient of equation (137) may now be expressed in terms of $X(0)^{(1)}$ as follow: Taking

$$- \frac{2^3 \hbar c \ (E_1 - E_0)^2 \left\langle r_1^2 \right\rangle \left\langle r_2^2 \right\rangle}{\pi^2 \, 3^2 \, (\hbar c)^4 \, R^3} = \frac{8 (E_1 - E_0)^3 \, R^3}{3 \, \pi^2 \, (\hbar c)^3} \times \left[\frac{- \left\langle r_1^2 \right\rangle \left\langle r_2^2 \right\rangle}{3 \, R^6 \, (E_1 - E_0)} \right] ,$$

equation (137) becomes

$$X(1)^{(1)} = \left[\frac{8 a^3 X(0)^{(1)}}{3 \pi^2}\right] \int_0^\infty b \, db \int_0^\infty \frac{\beta \, d\beta \, \{F(b) \ F(\beta) + 2 \, G(b) \ G(\beta)\}}{(b + \beta)} . \tag{138}$$

Applying similar modifications to the third term in equation (134) and remembering that the sums over i, j result in $(1 + \cos^2 \Theta)$, one obtains

$$X(2)^{(1)} = \frac{(E_1 - E_0)^3 \left\langle r_1^2 \right\rangle \left\langle r_2^2 \right\rangle}{2^4 \, \pi^4 \, (c\hbar)^3 \, (3)^2} \int_0^\infty \kappa \, d\kappa \int_0^\infty \kappa' \, d\kappa' \left(\frac{1}{\kappa + \kappa'}\right) \int d\Omega_\kappa \int d\Omega_{\kappa'}$$

$$\times \{1 + \cos^2 \Theta\} \left\{ \frac{e^{-i(\vec{\kappa} + \vec{\kappa}') \cdot \vec{R}}}{\left[(E_1 - E_0) + \hbar c \kappa\right]} + \frac{e^{+i(\vec{\kappa} + \vec{\kappa}') \cdot \vec{R}}}{\left[(E_1 - E_0) + \hbar c \kappa'\right]} \right.$$

$$\left. + \frac{\hbar c \ (\kappa + \kappa') \ e^{-i(\vec{\kappa} - \vec{\kappa}') \cdot \vec{R}}}{\left[(E_1 - E_0) + \hbar c \kappa\right]\left[(E_1 - E_0) + \hbar c \kappa'\right]} \right\} . \tag{139}$$

Evaluating the integrals over $d\Omega$ using results in Appendix B and using the same definitions, the denominators in equation (138) may be modified to give

$$X(2)^{(1)} = -\frac{8a^4 X(0)^{(1)}}{3\pi^2} \int_0^\infty b\,db \int_0^\infty \beta\,d\beta \left(\frac{1}{b+\beta}\right) \left[F(b)\,F(\beta) + 2\,G(b)\,G(\beta)\right]$$

$$\times \left\{ \frac{1}{(a+b)} + \frac{1}{(a+\beta)} + \frac{(b+\beta)}{(a+b)(a+\beta)} \right\} \quad . \tag{140}$$

The next term to be evaluated is given by

$$X(3)^{(1)} = \left[-\frac{(E_1 - E_0)^2}{2\pi^2 \hbar c} \right] \int_0^\infty \kappa\,d\kappa \left[\frac{1}{(E_1 - E_0)\left[(E_1 - E_0) + \hbar c\kappa\right]} + \frac{-1}{\left[(E_1 - E_0) + \hbar c \kappa\right]^2} \right]$$

$$\times \int d\Omega_\kappa\, e^{-i\vec{\kappa}\cdot\vec{R}} \sum_{ij} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j \right\} \left\langle \bar{H}_q^{(2)} \; (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle \quad . \tag{141}$$

To consider the sum over i, j, one defines $\left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j \right\}$ as $\mathcal{P}_{ij}$. Substituting for $H_q^{(2)}$ from equation (3) this term gives

$$\sum_{ij} \mathcal{P}_{ij} \left\langle H_q^{(2)} \; (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle$$

$$= \sum_{ij} \mathcal{P}_{ij} \sum_{L_1} \sum_{L_2} \sum_{m} \frac{(-1)^{L_2} (4\pi)\,(L_1 + L_2)!}{R^{L_1+L_2+1} \left\{(2L_1+1)(2L_2+1)\right\}^{1/2}} \left\langle r_1^{L_1+1} \right\rangle \left\langle r_2^{L_2+1} \right\rangle$$

$$\times \frac{1}{\left\{(L_1+m)!\,(L_1-m)!\,(L_2-m)!\,(L_2+m)!\right\}^{1/2}} \left\langle (\vec{r}_1)_i \, Y_{L_1}^{m^*}(\mathrm{I}) \right\rangle \left\langle (\vec{r}_2)_j \, Y_{L_2}^{-m^*}(\mathrm{II}) \right\rangle \tag{142}$$

The matrix elements containing $(\vec{r})_i$ and Y_L^M are evaluated by taking each of the components $(\vec{r}_1)_i$ expressed in terms of Spherical Harmonics; the results are:

$$\left\langle (\hat{r}_1)_i \, Y_{L_1}^{m^*}(1) \right\rangle \Big|_{i=1} = \frac{1}{4\pi} \sqrt{\frac{2\pi}{3}} \left(\delta_{m,-1} - \delta_{m,+1} \right) \delta_{L_1,+1} \quad ,$$

$$\left\langle (\hat{r}_1)_i \, Y_{L_1}^{m^*}(1) \right\rangle \Big|_{i=2} = \frac{i}{4\pi} \sqrt{\frac{2\pi}{3}} \left(\delta_{M,-1} + \delta_{m,+1} \right) \delta_{L_1,+1} \quad ,$$

$$\left\langle (\hat{r}_1)_i \, Y_{L_1}^{m^*}(1) \right\rangle \Big|_{i=3} = \frac{1}{4\pi} \sqrt{\frac{2\pi}{3}} \left(\delta_{M,0} \, \delta_{L_1,+1} \right) \quad ; \qquad (143)$$

and similar results are obtained for $(\vec{r}_2)_i$. Noting that the L_1, L_2 values are restricted to $L_1 = L_2 = 1$, equation (142) reduces to

$$\sum_{ij} \mathcal{P}_{ij} \left\langle H_q^{(2)} \; (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle$$

$$= \left[\frac{(-2)\,(4\pi) \left\langle r_1^2 \right\rangle \left\langle r_2^2 \right\rangle}{3\,R^3} \right] \sum_{m=-1}^{+1} \left[\frac{1}{(1+m)!\,(1-m)!} \right]$$

$$\times \sum_{ij} \mathcal{P}_{ij} \left\langle (\hat{r}_1)_i \, Y_1^{m^*}(1) \right\rangle \left\langle (\hat{r}_2)_j \, Y_1^{-m^*}(2) \right\rangle \quad . \qquad (144)$$

Performing the above sum over i, j and the matrix multiplications, one obtains

$$\sum_{ij} \mathcal{P}_{ij} \left\langle H_q^{(2)} \; (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle = \frac{(-2)\,(4\pi) \left\langle r_1^2 \right\rangle \left\langle r_2^2 \right\rangle}{3\,R^3\,(4\pi)^2}$$

$$\times \left\{ \left(-\frac{2\pi}{3} \right) \mathcal{P}_{11} + \left(-\frac{2\pi}{3} \right) \mathcal{P}_{22} + \left(\frac{4\pi}{3} \right) \mathcal{P}_{3,3} \right\}$$

$$= \left(\frac{1}{3} \right) \left\langle r_1^2 \right\rangle \left(\frac{1}{3} \right) \left\langle r_2^2 \right\rangle \left(\frac{1}{R^3} \right) \left\{ 3 \cos^2 \left[(\hat{\kappa})_3, (\hat{\kappa})_3 \right] - 1 \right\} \quad . \qquad (145)$$

Substituting this in equation (141) and redefining the constant terms yields

$$X(3)^{(1)} = \frac{a^3 X(0)^{(1)}}{(3)(2\pi^2)} \int_0^\infty b\,db \left[\frac{1}{a(a+b)} - \frac{1}{(a+b)^2}\right] \int d\Omega_\kappa \, e^{i\vec{\kappa}\cdot\vec{R}} \left\{3\cos^2\theta_\kappa - 1\right\} \quad . \qquad (146)$$

Performing the integration over θ_κ, ϕ_κ, using results in Appendix B the above equation simplifies to

$$X(3)^{(1)} = \frac{4a^3 X(0)^{(1)}}{3\pi} \int_0^\infty \frac{b^2\,db}{a(a+b)^2} \left\{F(b) + 2\,G(b)\right\} \quad . \qquad (147)$$

The last term in equation (134) is simplified considerably since the sums over i, j and ℓ, s collapse to $(1 + \cos^2 \Theta)$. Carrying out the integrations over $d\Omega$ and modifying the results as in previous terms, one obtains

$$X(4)^{(1)} = \frac{4a^5 X(0)^{(1)}}{3\pi^2} \int b\,db \int \beta\,d\beta \left\{F(b)\,F(\beta) + 2\,G(b)\,G(\beta)\right\}$$

$$\times \left\{ \frac{1}{(b+\beta)}\left[\frac{1}{(a+b)^2} + \frac{(2a+b+\beta)}{(a+b)(a+\beta)(2a)}\right] \right.$$

$$\left. + \frac{1}{(a+b)}\left[\frac{1}{2a\,(a+\beta)} + \frac{(2a+b+\beta)}{(a+b)(2a+b+\beta)(a+\beta)}\right] \right\} \quad . \qquad (148)$$

The above result may be expressed in a more symmetric form by rearranging the fractions as follows:

$$X(4)^{(1)} = \frac{4a^5 X(0)^{(1)}}{3\pi^2} \int_0^\infty b\,db \int_0^\infty \beta\,d\beta \left\{ F(b)\ F(\beta) + 2\,G(b)\ G(\beta) \right\}$$

$$\times \left\{ \left(\frac{1}{a+b}\right) \left[\frac{1}{(b+\beta)(a+b)} + \frac{1}{(a+b)(a+\beta)}\right] + \left(\frac{1}{a+b}\right)\left[\frac{1}{(b+\beta)(a+\beta)} + \frac{1}{a\,(a+\beta)}\right] \right\} . \quad (149)$$

Collecting terms, one obtains the following expression for the interaction energy $\Delta E/e^4$ to first order:

$$\Delta E_{d-d} = X(0)^{(1)} + X(1)^{(1)} + X(2)^{(1)} + X(3)^{(1)} + X(4)^{(1)} , \quad (150)$$

where the above quantities are defined in equations (133), (138), (140), (147), and (149). This expression gives us the interaction energy to first order expressed as groups of terms corresponding to various types of interactions. The reason for writing equation (150) in this form, as mentioned earlier, is to pinpoint the sources of the interaction energy. For instance, the first and fourth term $\left[X(0)^{(1)},\ X(3)^{(1)}\right]$ depend on the electrostatic interaction through its operator $H_q^{(2)}$; whereas, the other terms are independent of $H_q^{(2)}$. In addition, one notes that $X(3)^{(1)}$ is due to a mixture of electrostatic and field operators and the remainders are due to either the electrostatic operator $H_q^{(2)}$ or the field operators $\vec{A}\cdot\vec{P}$ and/or $\vec{A}\cdot\vec{A}$. These terms are discussed further in the following paragraphs.

Comparison with Previous Results

The expression given by equation (150) corresponds to the results reported by Casimir and Polder [1], and Power and Zienau [4]. Part of these results agree with those reported by Leech [2] in his attempt to solve this problem to first order. In particular, the term corresponding to $X(3)^{(1)}$ agrees with equation (29) of Leech's paper [2]. This may be seen by making appropriate substitutions of variables and constants as follows: $x \to b$, $X_1 \to X(0)^{(1)}$, and $\left\{F(b) + 2\,G(b)\right\} \to \frac{1}{x}\left(\sin x + \frac{3\cos x}{x} - \frac{3\sin x}{x^2}\right)$.

Agreement with Leech's work is also found for $X(1)^{(1)}$ to within a factor of 2 and with various terms contributing to $X(2)^{(1)}$ and $X(3)^{(1)}$. No further comparison is possible since he arranged his expressions differently than is done here. Leech's inability to verify Casimir and Polder's results is because of this error in $X(1)^{(1)}$ and because he obtained the limiting cases before doing the integrations over β. These integrations are required to show that equation (150) is indeed Casimir and Polder's result. This is done below to show the correctness of equation (150).

To perform the integrations over β in equation (150) one considers once more each one of the terms containing β integrals and then recombines the results to obtain an expression involving only integrals over b. The first element to be considered is $X(1)^{(1)}$ defined by equation (138). Rearranging factors yields the integral factor given by

$$\int_0^\infty b\,db\,F(b) \int_0^\infty \frac{\beta\,d\beta\,F(\beta)}{(b+\beta)} + 2\int_0^\infty b\,db\,G(b) \int_0^\infty \frac{\beta\,d\beta\,G(\beta)}{(b+\beta)} \quad . \tag{151}$$

These terms may be evaluated using the results given in Appendix C. For example, the first term above transforms into

$$\int_0^\infty b\,db\,F(b) \int_0^\infty \frac{\beta\,d\beta\,F(\beta)}{(b+\beta)} = 2\int_0^\infty b\,db\,F(b) \int_0^\infty \frac{\beta^2\,d\beta\,F(\beta)}{(\beta+b)(\beta-b)} \quad . \tag{152}$$

A similar transformation may be made in the integral containing $G(b)$ and $G(\beta)$. Using results given in Appendix C for the β integral in equation (152) and for the term containing the G function gives the desired results for the expression in (151). Substituting in $X(1)^{(1)}$ yields

$$X(1)^{(1)} = \frac{8a^3 X(0)^{(1)}}{3\pi^2}\left[\frac{\pi}{2i}\int_0^\infty \frac{db}{b^4}\left\{(b^2+3ib-3)\,e^{ib} - (b^2-3ib-3)\,e^{-ib}\right\}\right.$$

$$+\frac{\pi}{4i}\int_0^\infty \frac{db}{b^4}\left\{(b^4+2ib^3-5b^2-6ib+3)\,e^{2ib}\right.$$

$$\left.\left. - (b^4-2ib^3-5b^2+6ib+3)\,e^{-2ib}\right\}\right] . \tag{153}$$

The next element to be considered is $X(2)^{(1)}$ given by equation (140). To perform the β integration it is necessary to rearrange the fractional factors as follows:

$$\left(\frac{1}{b+\beta}\right)\left[\frac{1}{(a+b)}+\frac{1}{a+\beta}+\frac{(b+\beta)}{(a+b)(a+\beta)}\right]$$

$$=\left\{\frac{(a+b+a+\beta)}{(b+\beta)(a+b)(a+\beta)}+\frac{1}{(a+b)(a+\beta)}\right\}$$

$$=\left(\frac{2}{a+b}\right)\left\{\left[\frac{1}{(b+\beta)}+\frac{1}{(\beta-b)}\right]+\frac{b(a+b)+\beta(a+\beta)}{(b-\beta)(b+\beta)(a+\beta)}\right\} . \tag{154}$$

With this modification, $X(2)^{(1)}$ becomes

$$X(2)^{(1)} = -\frac{16a^4 X(0)^{(1)}}{3\pi^2}\int_0^\infty b\,db\int_0^\infty \beta\,d\beta\left\{F(b)\,F(\beta)+2\,G(b)\,G(\beta)\right\}$$

$$\times\left\{\frac{1}{(a+b)}\left(\frac{1}{b+\beta}+\frac{1}{\beta-b}\right)+\frac{b(a+b)+\beta(a+\beta)}{(a+b)(a+\beta)(b+\beta)(b-\beta)}\right\} . \tag{155}$$

By arranging the terms in this manner, one readily obtains the β integral of the second fraction. Analysis of this fraction shows that it is symmetric in b and β in all the factors except the one containing $(b-\beta)$. Interchanging b and β results in a change of sign. This feature is utilized by taking

$$\int_0^\infty b\,db \int_0^\infty \beta\,d\beta \left\{F(b)\ F(\beta) + 2\ G(b)\ G(\beta)\right\} \left[\frac{b(a+b) + \beta(a+\beta)}{(a+b)(a+\beta)(b+\beta)(b-\beta)}\right]$$

and separating the above quantity into two parts given by

$$\frac{1}{2}\int_0^\infty \ldots\ db \int_0^\infty \ldots\ d\beta + \frac{1}{2}\int_0^\infty \ldots\ db \int_0^\infty \ldots\ d\beta \quad ,$$

then interchanging b and β in the second half to obtain

$$\frac{1}{2}\int_0^\infty \ldots\ db \int_0^\infty \ldots\ d\beta - \frac{1}{2}\int_0^\infty \ldots\ db \int_0^\infty \ldots\ d\beta \quad .$$

Hence, one sees that this part of equation (155) gives a vanishing contribution. Using results in Appendix C, the other portion of equation (155) is integrated over β, resulting in

$$X(2)^{(1)} = -\frac{16 a^4 X(0)^{(1)}}{3\pi^2}\left[\frac{\pi}{2i}\int_0^\infty \frac{db}{b^4(a+b)}\left\{(b^2+3ib-3)\,e^{ib} - (b^2-3ib-3)\,e^{-ib}\right\}\right.$$
$$+\frac{\pi}{4i}\int_0^\infty \frac{db}{b^4(a+b)}\left\{(b^4+2ib^3-5b^2-6ib+3)\,e^{2ib}\right.$$
$$\left.\left. -(b^4-2ib^3-5b^2+6ib+3)\,e^{-2ib}\right\}\right] \quad . \tag{156}$$

$X(3)^{(1)}$ is already expressed in terms of an integral over b, hence, one only needs to replace $\left\{F(b) + 2\ G(b)\right\}$ by its definition. Thus, one obtains

$$X(3)^{(1)} = \frac{4a^3 X(0)^{(1)}}{3\pi^2}\left[\frac{\pi}{2i}\int \frac{b\,db}{b^3}\left[\frac{b}{a(a+b)^2}\right]\right.$$
$$\left.\times\left\{(b^2+3ib-3)\,e^{ib} - (b^2-3ib-3)\,e^{-ib}\right\}\right] \quad . \tag{157}$$

The next term to be considered is $X(4)^{(1)}$ defined by equation (149). Before performing the β integration it is necessary to rearrange the denominators involving b and β, in a manner similar to the one used in simplifying $X(2)^{(1)}$. In doing this, one is guided by the symmetry displayed by the quantities involving b's and β's. Considering the fractions in equation (149) and rearranging factors yields

$$\left\{ \left(\frac{1}{a+b}\right) \left[\frac{1}{(b+\beta)(a+\beta)} + \frac{1}{(a+b)(a+\beta)}\right] \right.$$

$$\left. + \left(\frac{1}{a+b}\right) \left[\frac{1}{(b+\beta)(a+\beta)} + \frac{1}{a(a+\beta)}\right] \right\}$$

$$= \left\{ \frac{(2a+b)}{a(a+b)^2} \left[\frac{1}{(b+\beta)} + \frac{1}{(\beta-b)}\right] + \frac{a(b+\beta) + \beta(a+\beta) + b(a+b)}{a(a+b)(a+\beta)(b+\beta)(b-\beta)} \right\} . \tag{158}$$

The last term in the right-hand side of equation (158) is symmetric in b and β in all terms except $(b-\beta)$. Performing the same operations leading up to equation (156), indicates that the second term in equation (158) does not contribute to the β integration of equation (149). Hence, considering only the first term in equation (158), $X(4)^{(1)}$ becomes

$$X(4)^{(1)} = \left[\frac{4a^5 X(0)^{(1)}}{3\pi^2}\right] \int_0^\infty b\,db \int_0^\infty \beta\,d\beta \left[F(b)\,F(\beta) + 2\,G(b)\,G(\beta)\right]$$

$$\times \left\{ \frac{(2a+b)}{a(a+b)^2} \left[\frac{1}{b+\beta} + \frac{1}{\beta-b}\right] \right\} . \tag{159}$$

Recombining the above factors shows that the β integrals are the same as in the first term of equation (155). Using results obtained in Appendix C, $X(4)^{(1)}$ becomes

$$X(4)^{(1)} = \frac{4a^5 X(0)^{(1)}}{3\pi^2} \int_0^\infty \frac{(2a+b)\,b\,db}{a(a+b)^2 b^5}$$

$$\times \left\{ \frac{\pi}{2i} \left[(b^2 + 3ib - 3)\, e^{ib} - (b^2 - 3ib - 3)\, e^{-ib} \right] \right.$$

$$+ \frac{\pi}{4i} \left[(b^4 + 2ib^3 - 5b^2 - 6ib + 3)\, e^{2ib} \right.$$

$$\left. \left. - (b^4 - 2ib^3 - 5b^2 + 6ib + 3)\, e^{-2ib} \right] \right\} . \qquad (160)$$

With all the terms in equation (150) given in terms of integrals over b and $X(0)^{(1)}$ as coefficient, the interaction energy correction ΔE_{d-d} may now be expressed as a function of these new terms by separating the integrals over $e^{\pm ib}$ and $e^{\pm 2ib}$ as follows:

$$\Delta E_{d-d} = X(0)^{(1)} \left\{ 1 + \frac{4a^3}{3\pi} \int_0^\infty \frac{db}{ib^4} \left[1 - \frac{2a}{(a+b)} + \frac{b^2}{2} \left(\frac{b}{a(a+b)^2} \right) + \frac{a}{2} \left(\frac{2a+b}{(a+b)^2} \right) \right] \right.$$

$$\times \left[(b^2 + 3ib - 3)\, e^{ib} - (b^2 - 3ib - 3)\, e^{-ib} \right]$$

$$+ \frac{4a^3}{3\pi} \int_0^\infty \frac{db}{ib^4} \left[\frac{1}{2} - \frac{a}{(a+b)} + \frac{1}{4} \left(\frac{2a^2 + ab}{(a+b)^2} \right) \right]$$

$$\left. \times \left[(b^4 + 2ib^3 - 5b^2 - 6ib + 3)\, e^{2ib} - (b^4 - 2ib^3 - 5b^2 + 6ib + 3)\, e^{-2ib} \right] \right\} . \qquad (161)$$

Note that the first term of the above equation results when only the electrostatic interaction is considered; this yields the proper limiting case. By recombining the fractional quantities of the above terms, one obtains

$$\left\{ 1 - \frac{2a}{(a+b)} + \frac{b^2}{2} \left[\frac{b}{a(a+b)^2} \right] + \frac{1}{2} \left[\frac{2a^2 + ab}{(a+b)^2} \right] \right\} = \left(\frac{b}{2a} \right) .$$

Substituting into equation (161) yields the following expression for ΔE_{d-d} :

$$\Delta E_{d-d} = X(0)^{(1)} \left\{ 1 + \frac{4a^3}{3\pi} \int_0^\infty \frac{b\,db}{a b^4} \left[\frac{(b^2 + 3ib - 3)\, e^{ib}}{2i} - \frac{(b^2 - 3ib - 3)\, e^{-ib}}{2i} \right] \right.$$

$$+ \frac{4a^3}{3\pi} \int_0^\infty \frac{db}{2b^4} \left[\frac{b}{a} + \frac{-b^3}{a(a+b)^2} \right] \times \left[\frac{(b^4 + 2ib^3 - 5b^2 - 6ib + 3)\, e^{2ib}}{2i} \right.$$

$$\left. \left. - \frac{(b^4 - 2ib^3 - 5b^2 + 6ib + 3)\, e^{-2ib}}{2i} \right] \right\} . \tag{162}$$

This is essentially the Casimir and Polder result expressed in terms of complex quantities. The singularities appearing in the above expression present no problem, because when using stationary state perturbation theory to approximate physical situations, one takes the "principal value" of the sums or integrals appearing in the results. To transform equation (162) into real quantities, one considers a contour in the complex plane which includes the interval of integration in equation (162). This is done by taking appropriate contours which include the real axis. The first integral term in equation (162) is integrated by first considering its factors, as follows. Taking

$$\int_0^\infty \frac{db}{a b^3} \left[\frac{(b^2 + 3ib - 3)\, e^{ib}}{2i} - \frac{(b^2 - 3ib - 3)\, e^{-ib}}{2i} \right]$$

and letting $b \rightarrow -b$ in second integral, as well as exchanging appropriate limits of integration, results in the following expression

$$\int_{-\infty}^{+\infty} \frac{db}{a b^3} \frac{(b^2 + 3ib - 3)\, e^{ib}}{2i} .$$

The principal value of this integral is obtained by using the values given in Appendix C; the result is

$$\text{P.V.} \int_{-\infty}^{\infty} \frac{db}{a b^3} \frac{(b^2 + 3ib - 3)\, e^{ib}}{2i} = -\left(\frac{\pi}{4a}\right) .$$

The results for the other integral terms in equation (162) are

$$\text{P.V.} \int_0^\infty \frac{db}{2ab^3} \left[\frac{(b^4 + 2ib^3 - 5b^2 - 6ib + 3)\, e^{2ib}}{2i} - \frac{(b^4 - 2ib^3 - 5b^2 + 6ib + 3)\, e^{-2ib}}{2i} \right]$$

$$= \left(\frac{\pi}{4a} \right) ,$$

$$\text{P.V.} \int_0^\infty - \frac{db}{2ab(a+b)^2} \left[\frac{(b^4 + 2ib^3 - 5b^2 - 6ib + 3)\, e^{2ib}}{2i} - \frac{(b^4 - 2ib^3 - 5b^2 + 6ib + 3)\, e^{-2ib}}{2i} \right]$$

$$= - \left(\frac{3\pi}{4a^3} \right) + \int_0^\infty \frac{dy}{(a^2 + y^2)^2} (y^4 + 2y^3 + 5y^2 + 6y + 3)\, e^{-2y} \qquad ;$$

where $iy \equiv b$ in the integration containing e^{+2ib}, and $-iy = b$ in the *integration containing* e^{-2ib}. *(See Appendix C for details.) Combining* these results indicates that the contributions of the residues at the $\underline{b}$ origin cancel the contribution due to the electrostatic interaction $X(0)^{(1)}$. Hence, ΔE_{d-d} *becomes*

$$\Delta E_{d-d} = \frac{4a^3 X(0)^{(1)}}{3\pi} \int_0^\infty \frac{dy\,(y^4 + 2y^3 + 5y^2 + 6y + 3)\, e^{-2y}}{(a^2 + y^2)^2} . \quad (163)$$

Having ΔE_{d-d} in the above form allows one to compare results directly with those of Casimir and Polder as given by Power and Zienau in equation (28) of Reference 4. This is accomplished by letting $y \equiv uR$, $(E_1 - E_0)/\hbar c \equiv E$ and recombining the coefficient into dipole moment matrix elements. Making these substitutions, as well as using the definitions for $\underline{a}$, equation (163) becomes

$$\Delta E_{d-d} = \frac{4(E_1 - E_0)^3 R^3 X(0)^{(1)}}{(\hbar c)^3 \,(3\pi)} \int_0^\infty \frac{R\,(uR)^4\, du\, e^{-2Ru}}{R^4 \left\{ \left[\frac{(E_1 - E_0)}{\hbar c} \right]^2 + u^2 \right\}^2}$$

$$\times \left\{ 1 + \frac{2}{(uR)} + \frac{5}{(uR)^2} + \frac{6}{(uR)^3} + \frac{3}{(uR)^4} \right\} .$$

Replacing $X(0)^{(1)}$ in terms of the expression given in equation (133) yields

$$\Delta E_{d\text{-}d} = -\frac{4\,(E_1 - E_0)^2 \langle r_1^2 \rangle \langle r_2^2 \rangle}{3^2 \pi R^2 (\hbar c)^3} \int_0^\infty \frac{u^4\, du\, e^{-2Ru}}{\left[\left(\frac{E_1 - E_0}{\hbar c}\right)^2 + u^2\right]^2}$$

$$\times \left\{ 1 + \frac{2}{(uR)} + \frac{5}{(uR)^2} + \frac{6}{(uR)^3} + \frac{3}{(uR)^4} \right\} \quad . \qquad (164)$$

The integral form is in agreement with previous results. Comparison of equation (164) to equation (28) of Reference 4 shows that Power and Zienau omitted some factors of $\hbar c$. The reason may be that in part of their discussion they let $\hbar = c = 1$. Analysis of the rest of the factors in equation (164) is simplified by writing down equation (28) of Reference 4:

$$\Delta E^M = -\frac{4}{\pi} \frac{\langle q(1) \rangle^2 \langle q(2) \rangle^2 E^2}{\hbar c R^2} \int_0^\infty \frac{u^4\, e^{-2uR}\, du}{[E^2 + u^2]^2}$$

$$\times \left\{ 1 + \frac{2}{(uR)} + \frac{5}{(uR)^2} + \frac{6}{(uR)^3} + \frac{3}{(uR)^4} \right\} \quad . \qquad (165)$$

A comparison of this equation to equation (164) shows that if one lets $\frac{(E_1 - E_0)}{\hbar c} = E$, $(\hbar c)$ is left out in the fraction inside the integral. The dipole matrix elements $\langle q(1) \rangle^2$ correspond to $\frac{\langle r_1^2 \rangle}{3}$. Power and Zienau define this matrix element in equation (23) of Reference 4 as

$$\sum \left[q_{i0/\ell}(1)\, q_{j\ell/0}(1) \right] = \delta_{ij}\, \langle q(1) \rangle^2 \quad , \qquad (166)$$

where they take the sum over the intermediate 2p atomic states. This operation is equivalent to the relation used here, given by

$$\sum_m \left\langle \alpha \,\middle|\, (\vec{r}_1)_i \,\middle|\, m \right\rangle \left\langle m \,\middle|\, (\vec{r}_1)_j \,\middle|\, \alpha \right\rangle = \left\langle \alpha \,\middle|\, (\vec{r}_1)_i (\vec{r}_1)_j \,\middle|\, \alpha \right\rangle$$

$$= \frac{1}{3} \left\langle r_1^2 \right\rangle \delta_{ij} \quad ,$$

where m is summed over the 2p intermediate states. By letting $\vec{q} \equiv e\,\vec{r}$ and making the above comparison of matrix products, complete agreement is reached between the results obtained here and those given by Power and Zienau [4].

Since the main objective in this calculation is to obtain the form of the interaction energy to various multipole orders, a discussion of equation (164) will be given after the higher multipole order corrections are evaluated. There is a twofold reason for showing the detailed correspondence between the results obtained here and those of previous authors: (1) it shows that the overall procedure used here is correct, and (2) it provides the steps to be followed in subsequent calculations where a detailed discussion is not practical.

DIPOLE-QUADRUPOLE APPROXIMATIONS

Introduction

The dipole-quadrupole order corrections, ΔE_{d-q}, to the interaction energy given by ΔE are evaluated in this discussion. The term ΔE_{d-q} consists of the dipole-quadrupole order terms in the electrostatic interaction energy and the second set of terms in each of the X(i) expressions given previously.

Starting with the electrostatic interaction energy given by equation (85), one obtains the dipole-quadrupole order terms by setting $L_1 = 1$, $L_2 = 2$, $m = 0, \pm 1$ and $L_1 = 2$, $L_2 = 1$, $m = 0, \pm 1$. Performing these operations and defining these terms by $X(0)^{(2)}$ yields

$$X(0)^{(2)} = \frac{(-1)^4 \left\{ (1+2)! \right\}^2 \left\langle R_{1,0} \middle| r_1^2 \middle| R_{1,0} \right\rangle \left\langle R_{1,0} \middle| r_2^4 \middle| R_{1,0} \right\rangle}{R^8 \left\{ (3)(5)(2E_0 - 2E_1) \right\}}$$

$$\times \sum_{m=-1}^{+1} \left[\frac{1}{(1-m)!\,(1+m)!\,(2-m)!\,(2+m)!} \right]$$

$$+ \frac{(-1)^2 \left\{ (2+1)! \right\}^2 \left\langle R_{1,0} \middle| r_1^4 \middle| R_{1,0} \right\rangle \left\langle R_{1,0} \middle| r_2^2 \middle| R_{1,0} \right\rangle}{R^8 \left\{ (5)(3)(2E_0 - 2E_1) \right\}}$$

$$\times \sum_{m=-1}^{+1} \left[\frac{1}{(2-m)!\,(2+m)!\,(1-m)!\,(1+m)!} \right] \quad . \qquad (167)$$

After performing the summation and collecting terms, one obtains the following expression

$$X(0)^{(2)} = - \frac{\left\langle r_1^2 \right\rangle \left\langle r_2^4 \right\rangle}{R^8 \,(E_1 - E_0)} \quad . \qquad (168)$$

The next term corresponding to $X(1)^{(2)}$ is obtained from the second term in equation (122). After factors are rearranged, this term becomes

$$X(1)^{(2)} = \left[- \frac{\hbar}{(3)\,(2)^5 \pi^4 \mu^2 c^3} \right] \left(\left\langle r_1^2 \right\rangle + \left\langle r_2^2 \right\rangle \right) \int \kappa\, d\kappa \int \kappa'\, d\kappa' \left(\frac{1}{\kappa + \kappa'} \right)$$

$$\times \int d\Omega_\kappa \int d\Omega_{\kappa'} \left\{ 1 + \cos^2\Theta \right\} \left\{ (\kappa^2 + \kappa'^2) + 2\kappa\kappa' \cos\Theta \right\} e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \quad . \qquad (169)$$

Separating the coefficient of the above term and replacing $\left(\frac{1}{2\mu c^2}\right)\left(\frac{1}{2\mu c^2}\right)$ by $\left[\frac{\left\langle r_1^2 \right\rangle (E_1 - E_0)}{3(\hbar c)^2} \right] \left[\frac{\left\langle r_2^2 \right\rangle (E_1 - E_0)}{3(\hbar c)^2} \right]$, one obtains the following expression for the above coefficient:

$$\left\{ \frac{(\hbar c) \left\langle r_1^2 \right\rangle \left\langle r_1^2 \right\rangle \left\langle r_2^2 \right\rangle (E_1 - E_0)^2}{(3)^3\,(2)^3\,\pi^4\,(\hbar c)^4} + \frac{(\hbar c) \left\langle r_2^2 \right\rangle \left\langle r_2^2 \right\rangle \left\langle r_1^2 \right\rangle (E_1 - E_0)^2}{(3)^3\,(2)^3\,\pi^4\,(\hbar c)^4} \right\} . \qquad (170)$$

Using equation (86), one obtains the relations

$$\langle r^2\rangle = \frac{(4!)}{2}\left(\frac{a_0}{2\,Z}\right)^2 ; \quad \langle r^4\rangle = \frac{(6!)}{2}\left(\frac{a_0}{2\,Z}\right)^4 ;$$

$$\langle r^2\rangle\langle r^2\rangle = \frac{2\langle r^4\rangle}{5} ;$$

which may be used to simplify the coefficient given in expression (170), as follows:

$$\frac{(2)\,(E_1 - E_0)^2}{(5)\,(3)^3\,(2)^3\,\pi^4\,(\hbar c)^3}\left(\left\langle r_1^4\right\rangle\left\langle r_2^2\right\rangle + \left\langle r_1^2\right\rangle\left\langle r_2^4\right\rangle\right) \quad .$$

By using results in Appendix B for the integrals over $d\Omega$ and substituting for κ and κ' using previous definitions, equation (169) becomes

$$X(1)^{(2)} = -\frac{2^4\,a^3\,X(0)^{(2)}}{(5)\,(3)^3\,\pi^2}\int_0^\infty b\,db\int_0^\infty \beta\,d\beta\left(\frac{1}{b+\beta}\right)$$
$$\times\left\{(b^2+\beta^2)\left[F(b)\;F(\beta) + 2\,G(b)\;G(\beta)\right]\right.$$
$$\left. - 2\,b\beta\,\frac{\left[\mathcal{F}(b)\;\mathcal{F}(\beta) + 4\,F_3(b)\;F_3(\beta)\right]}{b\beta}\right\} \quad . \tag{171}$$

In Appendix C the β integrals for this expression are evaluated as follows

$$X(1)^{(2)} = -\frac{2^4 a^3 X(0)^{(2)}}{(5)(3)^3 \pi^2}\left\{2\int b^3\,db\int \frac{\beta^2 d\beta\left[F(b)\ F(\beta) + 2\,G(b)\ G(\beta)\right]}{(\beta+b)(\beta-b)}\right.$$

$$+\,2\int b\,db\int \frac{\beta^4 d\beta\left[F(b)\ F(\beta) + 2\,G(b)\ G(\beta)\right]}{(\beta+b)(\beta-b)}$$

$$\left.-\,4\int b\,db\int \frac{\beta^2 d\beta\left[\mathcal{F}(b)\ \mathcal{F}(\beta) + 4\,F_3(b)\ F_3(b)\right]}{(\beta+b)(\beta-b)}\right\}$$

$$= -\frac{2^4 a^3 X(0)^{(2)}}{(5)(3)^3 \pi}\left[\int_0^\infty b\,db\left\{\left[F(b) + 2\,G(b)\right] + \frac{6}{b^2}\left[\mathcal{F}(b) - 4\,F_3(b)\right]\right\}\right.$$

$$+\,2i\int_0^\infty b^4\,db\left\{\left[F(b)\ F^+(b) + 2\,G(b)\ G^+(b)\right]\right.$$

$$\left.\left.-\frac{1}{b^2}\left[\mathcal{F}(b)\ \mathcal{F}^-(b) + 4\,F_3(b)\ F_3^+(b)\right]\right\}\right]; \qquad (172)$$

where

$$F(b) = \frac{1}{b^3}\left(\frac{[b^2 + ib - 1]\ e^{ib}}{2i} - \frac{[b^2 - ib - 1]\ e^{-ib}}{2i}\right),$$

$$F^+(b) = \frac{1}{b^3}\left(\frac{[b^2 + ib - 1]\ e^{ib}}{2i} + \frac{[b^2 - ib - 1]\ e^{-ib}}{2i}\right),$$

$$F_3(b) = \frac{1}{b^3}\left(\frac{[b^2 + 3ib - 3]\ e^{ib}}{2i} - \frac{[b^2 - 3ib - 3]\ e^{-ib}}{2i}\right)$$

$$F_3^+(b) = \frac{1}{b^3}\left(\frac{[b^2 + 3ib - 3]\ e^{ib}}{2i} + \frac{[b^2 - 3ib - 3]\ e^{-ib}}{2i}\right),$$

$$G(b) = \frac{1}{b^3}\left(\frac{[ib - 1]\ e^{ib}}{2i} - \frac{[-ib - 1]\ e^{-ib}}{2i}\right),$$

$$G^{+}(b) = \frac{1}{b^3}\left(\frac{[ib-1]\,e^{ib}}{2i} + \frac{[-ib-1]\,e^{-ib}}{2i}\right) ,$$

$$\mathcal{F}(b) = \frac{1}{b^3}\left(\frac{[ib^3-2b^2-3ib+3]\,e^{ib}}{2i} + \frac{[ib^3+2b^2-3ib-3]\,e^{-ib}}{2i}\right) ,$$

$$\mathcal{F}^{-}(b) = \frac{1}{b^3}\left(\frac{[ib^3-2b^2-3ib+3]\,e^{ib}}{2i} - \frac{[ib^3+2b^2-3ib-3]\,e^{-ib}}{2i}\right) .$$

Using these definitions, the result for $X(1)^{(2)}$ is quite compact. In addition, the products $F(b)\,F^{+}(b)$, $\mathcal{F}(b)\,\mathcal{F}^{-}(b)$, ... etc. are just the difference of two squares, since the binomials merely change sign in the second term.

The next term to be evaluated is $X(2)^{(2)}$ given by the second group of factors of $X(2)$ defined in equation (127). Expressing the coefficient of this expression in terms of $\langle r_1^2\rangle$ and $\langle r_2^2\rangle$, one obtains

$$\begin{aligned} X(2)^{(2)} = {} & \frac{(E_1-E_0)^3\langle r_1^2\rangle}{2^2\pi^4(\hbar c)^3(3)} \int \frac{d\vec{\kappa}}{\kappa} \int \frac{d\vec{\kappa}'}{\kappa'} \sum_{ij} \left\{\delta_{ij} - (\hat{\kappa})_i(\hat{\kappa})_j - (\hat{\kappa}')_i(\hat{\kappa}')_j + (\hat{\kappa})_i(\hat{\kappa}')_j(\hat{\kappa}\cdot\hat{\kappa}')\right\} \\ & \times \left[\left\{\frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa+\kappa')\left[(E_1-E_0)+\hbar c\kappa\right]} + \frac{e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa+\kappa')\left[(E_1-E_0)+\hbar c\kappa'\right]}\right\}\right. \\ & \times\left(-\frac{1}{2}\sum_{ts}\left\{\left(\frac{1}{3}\right)^2\langle r_1^2\rangle\langle r_2^2\rangle\omega_t\,\omega_s\,\delta_{ts}\,\delta_{ij} + \omega_t\,\omega_s\left\langle(\vec{r}_2)_t(\vec{r}_2)_s(\vec{r}_2)_i(\vec{r}_2)_j\right\rangle\right\}\right) \\ & + \left\{\frac{\hbar c\,e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1-E_0)+\hbar c\kappa\right]\left[(E_1-E_0)+\hbar c\kappa'\right]}\right\} \\ & \left.\times\left(-\frac{1}{2}\sum_{ts}\left\{\left(\frac{1}{3}\right)^2\langle r_1^2\rangle\langle r_2^2\rangle v_t\,v_s\,\delta_{ts}\,\delta_{ij} + v_t\,v_s\left\langle(\vec{r}_2)_t(\vec{r}_2)_s(\vec{r}_2)_i(\vec{r}_2)_j\right\rangle\right\}\right)\right] . \end{aligned} \tag{173}$$

The sums over i, j and t, s are evaluated using the same techniques as outlined previously. The results for the various terms are as follows:

$$\sum_{ij}\left\{\delta_{ij}-(\hat{\kappa})_i(\hat{\kappa})_j-(\hat{\kappa}')_i(\hat{\kappa}')_j+(\hat{\kappa})_i(\hat{\kappa}')_j(\hat{\kappa}\cdot\hat{\kappa}')\right\}\left(-\frac{1}{2}\right)\sum_{ts}\left(\frac{1}{3}\right)^2\left\langle r_1^2\right\rangle\left\langle r_2^2\right\rangle\omega_t\,\omega_s\,\delta_{ts}\,\delta_{ij}$$

$$=\left(-\frac{1}{2}\right)\left(\frac{1}{3}\right)^2\left\langle r_1^2\right\rangle\left\langle r_2^2\right\rangle\left\{(\kappa^2+\kappa'^2)(1+\cos^2\Theta)+2\,\kappa\kappa'\,(\cos\Theta+\cos^3\Theta)\right\}\quad,$$

$$\sum_{ij}\left\{\delta_{ij}-(\hat{\kappa})_i(\hat{\kappa})_j-(\hat{\kappa}')_i(\hat{\kappa}')_j+(\hat{\kappa})_i(\hat{\kappa}')_j(\hat{\kappa}\cdot\hat{\kappa}')\right\}\left(-\frac{1}{2}\right)\sum_{ts}\omega_t\,\omega_s\left\langle(\vec{r}_2)_t(\vec{r}_2)_s(\vec{r}_2)_i(\vec{r}_2)_j\right\rangle$$

$$=\left(-\frac{1}{2}\right)\left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\left\langle r_2^4\right\rangle\left\{(\kappa^2+\kappa'^2)(1+\cos^2\Theta)+4\,\kappa\kappa'\cos^3\Theta\right\}\quad. \qquad 174)$$

The terms containing the v_t, v_s factors have a similar form with only a minus sign in front of the factors $2\,\kappa\kappa'\,(\cos\Theta+\cos^3\Theta)$ and $4\,\kappa\kappa'\cos^3\Theta$. The evaluation of these sums is very lengthy and will not be given here. The procedure is simply to carry out the sums over t, s first and then over i, j. When matrix elements of the form $\left\langle(\vec{r}_2)_t(\vec{r}_2)_s(\vec{r}_2)_i(\vec{r}_2)_j\right\rangle$ are included, the best procedure is to evaluate the various combinations, using the fact that the result is invariant under interchange of t, s, i, j. Hence, the number of matrix elements that need to be evaluated is reduced considerably. For instance, in this case only 15 of the 36 possible terms need be evaluated. Of these, only 6 are nonzero and are given by

$$\left\langle(\vec{r})_i(\vec{r})_i(\vec{r})_i(\vec{r})_i\right\rangle=\frac{1}{5}\left\langle r^4\right\rangle\,,\qquad i=1,2,3,$$

$$\left\langle(\vec{r})_1(\vec{r})_1(\vec{r})_2(\vec{r})_2\right\rangle=\left\langle(\vec{r})_1(\vec{r})_1(\vec{r})_3(\vec{r})_3\right\rangle$$

$$\left\langle(\vec{r})_1(\vec{r})_1(\vec{r})_3(\vec{r})_3\right\rangle=\left\langle(\vec{r})_2(\vec{r})_2(\vec{r})_3(\vec{r})_3\right\rangle=\left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\left\langle r^4\right\rangle\,. \qquad (175)$$

Having evaluated the matrix elements, it is much easier to calculate the sums, since all the zero terms can be systematically excluded, allowing one to obtain the above results. This procedure is used in the equations to follow. The integrations over $d\Omega$ are done using the results in Appendix B and using the fact that the integrals over $(1+\cos^2\Theta)\,e^{\pm i\,(\vec{\kappa}+\vec{\kappa}')}$ give the same result. In addition, one finds that the integrals over $\cos\Theta$ and $\cos^3\Theta$ are related as follows:

$$\int\int (\cos\Theta + \cos^3\Theta)\, e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}\, d\Omega_\kappa\, d\Omega_{\kappa'}$$

$$= - \int\int (\cos\Theta + \cos^3\Theta)\, e^{\pm(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}\, d\Omega_\kappa\, d\Omega_{\kappa'} \quad . \tag{176}$$

The significance of this result cannot be over estimated since the negative sign introduced by the factors containing v_t, v_s is exactly offset by the integrals over $d\Omega_\kappa$, $d\Omega_{\kappa'}$. Incorporating this simplification in equation (173) and using previous definitions as well as performing the integrations over $d\Omega$, one obtains the following for equation (176).

$$X(2)^{(2)} = \frac{a^3 \langle r_1^2 \rangle}{(3)\,(2)^2 \pi^4 \hbar c R^7} \int b\,db \int \beta\, d\beta \left(\frac{1}{b+\beta}\right)$$

$$\times \left\{ \frac{1}{(a+b)} + \frac{1}{(a+\beta)} + \frac{(b+\beta)}{(a+b)\,(a+\beta)} \right\}$$

$$\times \left\{ \left(-\frac{1}{2}\right)\left(\frac{1}{3}\right)^2 \langle r_1^2\rangle\langle r_2^2\rangle \left((b^2+\beta^2)\,(2^5\pi^2) \left[F(b)\ F(\beta) + 2\,G(b)\ G(\beta)\right] \right.\right.$$

$$\left. + 2b\beta\,(-2^5\pi^2)\, \frac{\left[\mathcal{F}(b)\ \mathcal{F}(\beta) + 4\ F_3(b)\ F_3(\beta)\right]}{b\beta} \right)$$

$$+ \left(-\frac{1}{2}\right)\left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\langle r_2^4\rangle \left((b^2+\beta^2)\,(2^5\pi^2)\left[F(b)\ F(\beta) + 2\ G(b)\ G(\beta)\right] \right.$$

$$\left.\left. + 4b\beta\,(-2^4\pi^2)\left[\frac{\mathcal{F}_2(b)\ \mathcal{F}_2(\beta) + 6\,F_3(b)\ F_3(\beta)}{b\beta}\right] \right) \right\} , \tag{177}$$

where

$$F_3(b) \equiv F(b) + 2\ G(b),\ \ \mathcal{F}(b) = b^2 G(b) - F_3(b),\ \ \mathcal{F}_2(b) = b^2 G(b) - 2\ F_3(b) \quad .$$

To express the above results in terms of $X(0)^{(2)}$, one uses the relations between $\langle r^2 \rangle$ and $\langle r^4 \rangle$ given previously. Hence, the above coefficients may be rearranged as follows:

$$\frac{a^3 \langle r_1^2 \rangle (2^5 \pi^2)}{(3)(2)^2 \pi^4 R^7 (\hbar c)} \left[\left(-\frac{1}{2}\right)\left(\frac{1}{3}\right)^2 \langle r_1^2 \rangle \langle r_2^2 \rangle \right] = \frac{(2)^3 a^4 X(0)^{(2)}}{(5)(3)^3 \pi^2}$$

$$\frac{a^3 \langle r_1^2 \rangle (2^5 \pi^2)}{(3)(2)^2 \pi^4 R^7 (\hbar c)} \left[\left(-\frac{1}{2}\right)\left(\frac{1}{3}\right)\left(\frac{1}{5}\right) \langle r_2^4 \rangle \right] = \frac{(2)^2 a^4 X(0)^{(2)}}{(5)(3)^2 \pi^4}$$

Using these coefficients, equation (177) may be written as

$$X(2)^{(2)} = \frac{(2)^2 a^4 X(0)^{(2)}}{(5)(3)^3 \pi^2} \int b\,db \int \beta\, d\beta \left(\frac{2}{a+b}\right)$$

$$\times \left[\left(\frac{1}{b+\beta} + \frac{1}{\beta - b}\right) + \frac{b(a+b) + \beta(a+\beta)}{(b-\beta)(b+\beta)(a+\beta)} \right]$$

$$\times \left\{ 5(b^2+\beta^2) \left[F(b)\ F(\beta) + 2\ G(b)\ G(\beta)\right] \right.$$

$$\left. - 2\left[2\,\mathcal{F}(b)\,\mathcal{F}(\beta) + 3\,\mathcal{F}_2(b)\,\mathcal{F}_2(\beta) + 26\,F_3(b)\,F_3(\beta)\right] \right\}. \qquad (178)$$

The β integrals are now evaluated using the results of Appendix C. Since the second fraction involving b's and β's has been shown not to contribute, only the first factor in equation (178) need be considered. Expanding, this quantity becomes

$$
\begin{aligned}
X(2)^{(2)} &= \frac{2^3 a^4 X(0)^{(2)}}{3^3 (5\pi^2)} \\
&\times \left\{ 10 \int_0^\infty \frac{b^3 db}{(a+b)} \int_0^\infty \frac{\beta^2 d\beta}{(b+\beta)(\beta - b)} \left[F(b)\ F(\beta) + 2\ G(b)\ G(\beta) \right] \right. \\
&+ 10 \int_0^\infty \frac{b\, db}{(a+b)} \int_0^\infty \frac{\beta^4 d\beta}{(b+\beta)(\beta - b)} \left[F(b)\ F(\beta) + 2\ G(b)\ G(\beta) \right] \\
&- 8 \int_0^\infty \frac{b\, db}{(a+b)} \int_0^\infty \frac{\beta^2 d\beta}{(b+\beta)(\beta - b)} \left[\mathcal{F}(b)\ \mathcal{F}(\beta) \right] \\
&- 12 \int_0^\infty \frac{b\, db}{(a+b)} \int_0^\infty \frac{\beta^2 d\beta}{(b+\beta)(\beta - b)} \left[\mathcal{F}_2(b)\ \mathcal{F}_2(\beta) \right] \\
&\left. - (4)(26) \int_0^\infty \frac{b\, db}{(a+b)} \int_0^\infty \frac{\beta^2 d\beta}{(b+\beta)(\beta - b)} \left[F_3(b)\ F_3(\beta) \right] \right\} . \qquad (179)
\end{aligned}
$$

By using previous results and values, obtained in Appendix C, the above expression reduces to

$$
\begin{aligned}
X(2)^{(2)} &= \frac{2^3 a^4 X(0)^{(2)}}{(3^3)(5)\pi} \\
&\times \left\{ \int_0^\infty \frac{b\, db}{a+b} \left[5\ F(b) + 10\ G(b) + \frac{12}{b^2}\ \mathcal{F}(b) + \frac{36}{b^2}\ \mathcal{F}_2(b) - \frac{(3)(52)}{b^2}\ F_3(b) \right] \right. \\
&+ i \int_0^\infty \frac{b^4 db}{a+b} \left[10\ F(b)\ F^+(b) + 20\ G(b)\ G^+(b) - \frac{4\ \mathcal{F}(b) \mathcal{F}^-(b)}{b^2} - \frac{6\ \mathcal{F}_2(b) \mathcal{F}_2^-(b)}{b^2} \right. \qquad (180) \\
&\left. \left. - \frac{(2)(26)\ F_3(b)\ F_3(b)}{b^2} \right] \right\} ,
\end{aligned}
$$

where

$$\mathcal{F}_2(b) = \frac{1}{b^3}\left[\frac{(i b^3 - 3 b^2 - 6 i b + 6)\, e^{i b}}{2i} + \frac{(i b^3 + 3 b^2 - 6 i b - 6)\, e^{-i b}}{2i}\right],$$

$$\mathcal{F}_2^-(b) = \frac{1}{b^3}\left[\frac{(i b^3 - 3 b^2 - 6 i b + 6)\, e^{i b}}{2i} - \frac{(i b^3 + 3 b^2 - 6 i b - 6)\, e^{-i b}}{2i}\right].$$

The next term to be considered is given by the second group of terms in X(3) defined by equation (129) and written here as

$$X(3)^{(2)} = \left[-\frac{4\,(E_1 - E_0)^2}{2^3\pi^2\hbar c}\right] \int_0^\infty \kappa\, d\kappa \int_0^\infty d\Omega_\kappa \sum_{ij} \left\{\delta_{ij} - (\hat{\kappa})_i(\hat{\kappa})_j\right\} e^{-i\vec{\kappa}\cdot\vec{R}}$$

$$\times \left\{\frac{1}{(E_1 - E_0)\left[(E_1 - E_0) + \hbar c\kappa\right]} + \frac{-1}{\left[(E_1 - E_0) + \hbar c\kappa\right]^2}\right\}$$

$$\times \left\{\left(-\frac{1}{2}\right) \sum_{ts} \kappa_t \kappa_s \left[\left\langle H_q^{(2)}\ (\vec{r}_1)_i(\vec{r}_2)_t(\vec{r}_2)_s(\vec{r}_2)_j\right\rangle - 2\left\langle H_q^{(2)}\ (\vec{r}_1)_t(\vec{r}_1)_i(\vec{r}_2)_s(\vec{r}_2)_j\right\rangle\right.\right.$$

$$\left.\left. + \left\langle H_q^{(2)}\ (\vec{r}_1)_t(\vec{r}_1)_s(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\right]\right\} \quad . \tag{181}$$

The above terms are evaluated using the same procedure used to obtain $X(3)^{(1)}$ except here one has no δ functions in the sums over t and s, to shorten the work. Before evaluating the terms in equation (181), one notes that the first and last terms involving $H_q^{(2)}$ may be combined by using the symmetry of the system. Interchanging the coordinates of atom I by the coordinates of atom II within the matrix elements of these two terms and expanding the sums over i, j and t, s, it can be shown that

$$\sum_{ij} \mathcal{P}_{ij} \sum_{ts} \left\langle H_q^{(2)}\ (\vec{r}_1)_i(\vec{r}_2)_t(\vec{r}_2)_s(\vec{r}_2)_j\right\rangle$$

$$= \sum_{ij} \mathcal{P}_{ij} \sum_{ts} \left\langle H_q^{(2)}\ (\vec{r}_1)_t(\vec{r}_1)_s(\vec{r}_1)_i(\vec{r}_2)_j\right\rangle \quad .$$

Hence, one needs to evaluate only two terms of equation (181). Rewriting these terms yields

$$\sum_{ij} \mathcal{P}_{ij} \sum_{ts} \kappa_t \kappa_s \left[\left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_i (\vec{r}_2)_s (\vec{r}_2)_j \right\rangle - \left\langle H_q^{(2)} (\vec{r}_1)_i (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_j \right\rangle \right].$$

Expanding the first term using the definition for $H_q^{(2)}$, one gets

$$\sum_{ij} \mathcal{P}_{ij} \sum_{ts} \kappa_t \kappa_s \sum_{L_1, L_2} \frac{(-1)^{L_2} (4\pi) (L_1 + L_2)! \left\langle r_1^{L_1+2} \right\rangle \left\langle r_2^{L_2+2} \right\rangle}{R^{L_1+L_2+1} \left\{ (2L_1 + 1)(2L_2 + 1) \right\}^{1/2}}$$
$$\times \sum_m \frac{\left\langle (\hat{r}_1)_i (\hat{r}_1)_t Y_{L_1}^{m^*} (1) \right\rangle \left\langle (\hat{r}_2)_j (\hat{r}_2)_s Y_{L_2}^{-m^*} (2) \right\rangle}{\left\{ (L_1 + m)! (L_1 - m)! (L_2 - m)! (L_2 + m)! \right\}^{1/2}} \quad . \qquad (182)$$

Since the summation indices i, t, j, s go over $1, 2, 3$, one needs to evaluate only six matrix elements of the form $\left\langle (\vec{r}_1)_i (\vec{r}_1)_t Y_{L_1}^{m^*} (1) \right\rangle$, because interchanging i and t does not affect the result. Expressing the $(\vec{r})_i$ components in terms of Spherical Harmonics, one obtains the following relations:

$$\left\langle (\vec{r})_1 (\vec{r})_1 Y_L^{m^*} \right\rangle = \frac{1}{4\pi} \sqrt{\frac{2\pi}{15}} \left(\delta_{m,+2} + \delta_{m,-2} - \sqrt{\frac{2}{3}}\, \delta_{m,0} \right) \delta_{L,+2} \quad ,$$

$$\left\langle (\vec{r})_2 (\vec{r})_2 Y_L^{m^*} \right\rangle = -\frac{1}{4\pi} \sqrt{\frac{2\pi}{15}} \left(\delta_{m,+2} + \delta_{m,-2} + \sqrt{\frac{2}{3}}\, \delta_{m,0} \right) \delta_{L,+2} \quad ,$$

$$\left\langle (\vec{r})_3 (\vec{r})_3 Y_L^{m^*} \right\rangle = \frac{2}{4\pi} \sqrt{\frac{(2)(2\pi)}{(3)(15)}}\, \delta_{m,0}\, \delta_{L,+2} \quad ,$$

$$\left\langle (\vec{r})_1 (\vec{r})_2 Y_L^{m^*} \right\rangle = \frac{i}{4\pi} \sqrt{\frac{2\pi}{15}} \left(\delta_{m,-2} - \delta_{m,+2} \right) \delta_{L,+2} \quad ,$$

$$\left\langle (\vec{r})_1 (\vec{r})_3 \, Y_L^{m*} \right\rangle = \frac{1}{4\pi} \sqrt{\frac{2\pi}{15}} \left(\delta_{m,-1} - \delta_{m,+1} \right) \delta_{L,+2} \quad ,$$

$$\left\langle (\vec{r})_2 (\vec{r})_3 \, Y_L^{m*} \right\rangle = \frac{i}{4\pi} \sqrt{\frac{2\pi}{15}} \left(\delta_{m,-1} + \delta_{m,+1} \right) \delta_{L,+2} \quad . \tag{183}$$

The significance of the above results is found in the $\delta_{L,+2}$ factor, which applies to both of the $(\vec{r_1})_i$ and $(\vec{r_2})_j$ type terms. This type of matrix element selects only the terms having $L_1 = L_2 = 2$ in the electrostatic interaction, and thus this term does not contribute to the dipole-quadrupole order interaction ($L_1 = 1$, $L_2 = 2$ or $L_1 = 2$, $L_2 = 1$). The reason for including it here is that it is of the right order in powers of $(\vec{r})_i$ and has the same general form as the other terms in equation (181). Since one is interested in the dipole-quadrupole type interaction, further evaluation of $\left\langle H_q^{(2)} \; (\vec{r_1})_t (\vec{r_1})_i (\vec{r_2})_s (\vec{r_2})_j \right\rangle$ is postponed until quadrupole-quadrupole order interactions are evaluated.

The next term to be considered is given by

$$\sum_{ij} \mathcal{P}_{ij} \sum_{ts} \kappa_t \kappa_s \sum_{L_1 L_2} \frac{(-1)^{L_2} (4\pi) (L_1 + L_2)! \left\langle r_1^{L_1+1} \right\rangle \left\langle r_2^{L_2+3} \right\rangle}{R^{L_1+L_2+1} \left\{ (2L_1 + 1)(2L_2 + 1) \right\}^{1/2}}$$

$$\times \sum_m \frac{\left\langle (\hat{r}_1)_i \, Y_{L_1}^{m*} (1) \right\rangle \left\langle (\hat{r}_2)_t (\hat{r}_2)_s (\hat{r}_2)_j \, Y_{L_2}^{-m*} (2) \right\rangle}{\left\{ (L_1 + m)! \, (L_1 - m)! \, (L_2 + m)! \, (L_2 - m)! \right\}^{1/2}} \quad . \tag{184}$$

The matrix elements $\left\langle (\vec{r_1})_i \, Y_{L_1}^{m*} \right\rangle$ have been evaluated and are given in equation (143). They are proportional to $\delta_{L_1,+1}$, which in turn picks out the lowest L value and the corresponding range in the sum over m in equation (184). The other matrix product has three $(\vec{r_2})_i$ components, each of which can take on three values; hence, one needs to evaluate every combination. The terms required are as follows:

$$\left\langle (\vec{r})_1 (\vec{r})_1 (\vec{r})_1 Y_{L_2}^{-m*} \right\rangle = \frac{1}{4\pi} \sqrt{\frac{\pi}{35}} \left(\delta_{m,+3} - \delta_{m,-3}\right) - \frac{1}{5}\sqrt{\frac{3\pi}{7}} \left(\delta_{m,+1} - \delta_{m,-1}\right) \delta_{L_2,+3}$$

$$+ \frac{1}{4\pi}\left(\frac{3}{5}\right)\sqrt{\frac{2\pi}{3}} \left(\delta_{m,+1} - \delta_{m,-1}\right)\delta_{L_2,+1} \quad ,$$

$$\left\langle (\vec{r})_1 (\vec{r})_1 (\vec{r})_2 Y_{L_2}^{-m*} \right\rangle = \frac{i}{4\pi} \left[\sqrt{\frac{\pi}{35}} \left(\delta_{m,+3} + \delta_{m,-3}\right) - \frac{1}{5}\sqrt{\frac{\pi}{(3)(7)}} \left(\delta_{m,+1} + \delta_{m,-1}\right)\right] \delta_{L_2,+3}$$

$$+ \frac{i}{4\pi}\left(\frac{1}{5}\right)\sqrt{\frac{2\pi}{3}} \left(\delta_{m,+1} + \delta_{m,-1}\right)\delta_{L_2,+1} \quad ,$$

$$\left\langle (\vec{r})_1 (\vec{r})_1 (\vec{r})_3 Y_{L_2}^{-m*} \right\rangle = \frac{1}{4\pi} \left[\sqrt{\frac{2\pi}{(15)(7)}} \left(\delta_{m,+2} + \delta_{m,-2}\right) - \frac{2}{5}\sqrt{\frac{\pi}{7}}\, \delta_{m,0}\right] \delta_{L_2,+3}$$

$$+ \frac{1}{4\pi}\left(\frac{1}{5}\right)\sqrt{\frac{4\pi}{3}}\, \delta_{m,0}\, \delta_{L_2,+1} \quad ,$$

$$\left\langle (\vec{r})_1 (\vec{r})_2 (\vec{r})_2 Y_{L_2}^{-m*} \right\rangle = -\frac{1}{4\pi} \left[\sqrt{\frac{\pi}{35}} \left(\delta_{m,+3} - \delta_{m,-3}\right) + \frac{1}{5}\sqrt{\frac{\pi}{(3)(7)}} \left(\delta_{m,+1} - \delta_{m,-1}\right)\right] \delta_{L_2,+3}$$

$$+ \frac{1}{4\pi}\left(\frac{1}{5}\right)\left(\sqrt{\frac{2\pi}{3}}\right)\left(\delta_{m,+1} - \delta_{m,-1}\right)\delta_{L_2,+1} \quad ,$$

$$\left\langle (\vec{r})_1 (\vec{r})_2 (\vec{r})_3 Y_{L_2}^{-m*} \right\rangle = \frac{i}{4\pi} \sqrt{\frac{2\pi}{(15)(7)}} \left(\delta_{m,+2} - \delta_{m,-2}\right)\delta_{L_2,+3} \quad ,$$

$$\left\langle (\vec{r})_1 (\vec{r})_3 (\vec{r})_3 Y_{L_2}^{-m*} \right\rangle = \frac{1}{4\pi}\left(\frac{4}{5}\right)\sqrt{\frac{\pi}{21}} \left(\delta_{m,+1} - \delta_{m,-1}\right)\delta_{L_2,+3}$$

$$+ \frac{1}{4\pi}\left(\frac{1}{5}\right)\sqrt{\frac{2\pi}{3}} \left(\delta_{m,+1} - \delta_{m,-1}\right)\delta_{L_2,+1} \quad ,$$

$$\left\langle (\vec{r})_2 (\vec{r})_2 (\vec{r})_2 Y_{L_2}^{-m*} \right\rangle = -\frac{i}{4\pi}\left[\sqrt{\frac{\pi}{35}} \left(\delta_{m,+3} + \delta_{m,-3}\right) + \frac{3}{5}\sqrt{\frac{\pi}{21}} \left(\delta_{m,-1} + \delta_{m,+1}\right)\right]\delta_{L_2,+3}$$

$$+ \frac{1}{4\pi}\left(\frac{3i}{5}\right)\sqrt{\frac{2\pi}{3}} \left(\delta_{m,+1} + \delta_{m,-1}\right)\delta_{L_2,+1} \quad ,$$

$$\left\langle (\vec{r})_2 (\vec{r})_2 (\vec{r})_3 Y_{L_2}^{-m*} \right\rangle = -\frac{1}{4\pi}\left[\sqrt{\frac{2\pi}{(15)(7)}} \left(\delta_{m,+2} + \delta_{m,-2}\right) - \frac{2}{5}\sqrt{\frac{\pi}{7}}\, \delta_{m,0}\right]\delta_{L_2,+3}$$

$$+ \frac{1}{4\pi}\left(\frac{2}{5}\right)\sqrt{\frac{\pi}{3}}\, \delta_{m,0}\, \delta_{L_2,+1} \quad ,$$

$$\left\langle (\vec{r})_2 (\vec{r})_3 (\vec{r})_3 Y_{L_2}^{-m*} \right\rangle = \frac{1}{4\pi}\left(\frac{4i}{5}\right)\sqrt{\frac{\pi}{21}} \left(\delta_{m,+1} + \delta_{m,-1}\right)\delta_{L_2,+3}$$

$$+ \frac{1}{4\pi}\left(\frac{i}{5}\right)\sqrt{\frac{2\pi}{3}} \left(\delta_{m,-1} + \delta_{m,+1}\right)\delta_{L_2,+1} \quad ,$$

$$\left\langle (\vec{r})_3 (\vec{r})_3 (\vec{r})_3 Y_{L_2}^{-m*} \right\rangle = \frac{1}{4\pi}\left(\frac{4}{5}\right)\sqrt{\frac{\pi}{7}}\, \delta_{m,0}\, \delta_{L_2,+3}$$

$$+ \frac{1}{4\pi}\left(\frac{6}{5}\right)\sqrt{\frac{\pi}{3}}\, \delta_{m,0}\, \delta_{L_1,+1} \quad . \tag{185}$$

Analysis of the preceding matrix elements shows that L_2 can be either 1 or 3. When referring to equation (184), one notes that the terms corresponding to dipole-quadrupole order are those for which $L_1 = L_2 = 1$. These terms give results proportional to $\langle r_1^2 \rangle \langle r_2^4 \rangle$ as required; hence, setting $L_1 = L_2 = 1$ in equation (184), one obtains the desired expression given by

$$\sum_{ij} \mathcal{P}_{ij} \sum_{ts} \kappa_t \kappa_s \left[\frac{(-1)(4\pi)(2)! \langle r_1^2 \rangle \langle r_2^4 \rangle}{3 R^3} \right]$$

$$\times \sum_{m=-1}^{+1} \frac{\left\langle (\hat{r}_1)_i Y_1^{m*}(1) \right\rangle \left\langle (\hat{r}_2)_t (\hat{r}_2)_s (\hat{r}_2)_j Y_1^{-m*}(2) \right\rangle}{(1+m)!(1-m)!}$$

$$= \frac{(-1)(4\pi)(2) \langle r_1^2 \rangle \langle r_2^4 \rangle}{3 R^3} \sum_{ij} \mathcal{P}_{ij} \sum_{ts} \kappa_t \kappa_s$$

$$\times \sum_{m} \frac{1}{(1+m)!(1-m)!} \left\langle (\hat{r}_1)_i Y_1^{m*}(1) \right\rangle \left\langle (\hat{r}_2)_t (\hat{r}_2)_s (\hat{r}_2)_j Y_1^{-m*}(2) \right\rangle . \tag{186}$$

The term corresponding to $L_1 = 1$, $L_2 = 3$ corresponds to quadrupole-quadrupole order interactions and will be considered later. Evaluation of equation (184) is rather involved since one needs to consider all the terms in the sums over i, j, t, s and m. Since the expression (185) consists of 10 different matrix elements and there are 3 possible factors $\left\langle (\vec{r}_1)_i Y_1^{m*}(1) \right\rangle$, one must consider 30 different products in equation (186). To show the procedure used in evaluating these terms, consider the matrix product corresponding to $i = t = s = j = 1$ in equation (186) which is given by

$$\left\langle (\hat{r}_1)_1 Y_1^{m*}(1) \right\rangle \left\langle (\hat{r}_2)_1 (\hat{r}_2)_1 (\hat{r}_2)_1 Y_1^{-m*}(2) \right\rangle = \frac{1}{4\pi} \sqrt{\frac{2\pi}{3}} \left(\delta_{m,-1} - \delta_{m,+1}\right) \left(\frac{1}{4\pi}\right) \left(\frac{3}{5}\right) \sqrt{\frac{2\pi}{3}} \left(\delta_{m,+1} - \delta_{m,-1}\right)$$

$$= \frac{(3)(2\pi)}{(4\pi)^2(5)} \left(\delta_{m,-1} - \delta_{m,+1}\right) \left(\delta_{m,+1} - \delta_{m,-1}\right) .$$

This result is obtained using equations (143) and (185). Substituting these values into equation (186), one obtains

$$\frac{(-1)(4\pi)(2)}{3R^3}\left\langle r_1^2\right\rangle\left\langle r_2^4\right\rangle\sum_m \frac{\mathcal{P}_{11}(\kappa_1\kappa_1)(3)(2\pi)}{(1+m)!\,(1-m)!\,(4\pi)^2(5)(3)}\left(\delta_{m-1}-\delta_{m,+1}\right)\left(\delta_{m,+1}-\delta_{m,-1}\right)$$

$$=\frac{(-1)\left\langle r_1^2\right\rangle\left\langle r_2^4\right\rangle}{(5)(3)\,R^3}\,\mathcal{P}_{11}(\kappa_1\kappa_1)\sum_m -\frac{\left(\delta_{m,+1}-\delta_{m,-1}\right)^2}{(1+m)!\,(1-m)!}$$

$$=\frac{\left\langle r_1^2\right\rangle\left\langle r_2^4\right\rangle}{(3)(5)R^3}\,(\kappa_1\kappa_1)\left\{1-(\hat{\kappa})_1(\hat{\kappa})_1\right\}\quad . \tag{187}$$

Performing this group of operations for each matrix product and defining this product as $\langle i\rangle\langle t,s,j\rangle$, one obtains all the elements of equation (186). Once all the terms are known, the sum over i, j, t, s may be performed and the final result recorded. An alternate method is afforded by expanding all the sums and then evaluating each product. This is not the shortest way since a number of matrix products $\langle i\rangle\langle t,s,j\rangle$ prove to be identically zero, making the expansion of the sums much easier. After evaluation of all these factors, one finds that the following are nonzero elements.

$$\langle 1\rangle\ \langle 1,1,1\rangle = \frac{\langle r_1^2\rangle\langle r_2^4\rangle}{(3)(5)\ R^3}\quad ,$$

$$\langle 1\rangle\ \langle 1,2,2\rangle = \frac{1}{3}\left[\frac{\langle r_1^2\rangle\langle r_2^4\rangle}{(3)(5)\ R^3}\right]\quad ,$$

$$\langle 1\rangle\ \langle 1,3,3\rangle = \frac{1}{3}\left[\frac{\langle r_1^2\rangle\langle r_2^4\rangle}{(3)(5)\ R^3}\right]\quad ,$$

$$\langle 2\rangle\ \langle 2,2,2,\rangle = \frac{1}{3}\left[\frac{\langle r_1^2\rangle\langle r_2^4\rangle}{(3)(5)\ R^3}\right]\quad ,$$

$$\langle 2\rangle\ \langle 2,1,1,\rangle = \frac{1}{3}\left[\frac{\langle r_1^2\rangle\langle r_2^4\rangle}{(3)(5)\ R^3}\right]\quad ,$$

$$\langle 2\rangle \langle 2,3,3,\rangle = \frac{1}{3}\left[\frac{\langle r_1^2\rangle\langle r_2^4\rangle}{(3)\,(5)\; R^3}\right] \quad ,$$

$$\langle 3\rangle \langle 3,3,3,\rangle = -\frac{6}{3}\left[\frac{\langle r_1^2\rangle\langle r_2^4\rangle}{(3)\,(5)\; R^3}\right] \quad ,$$

$$\langle 3\rangle \langle 3,1,1,\rangle = -\frac{2}{3}\left[\frac{\langle r_1^2\rangle\langle r_2^4\rangle}{(3)\,(5)\, R^3}\right] \quad ,$$

$$\langle 3\rangle \langle 3,2,2,\rangle = -\frac{2}{3}\left[\frac{\langle r_1^2\rangle\langle r_2^4\rangle}{(3)\,(5)\; R^3}\right] \quad . \tag{188}$$

With these results the sums over i, j, t, s, in equation (186) are now evaluated. After combining the various κ_t components and $(\hat{\kappa})_i$ unit vectors, one obtains[11]

$$\begin{aligned}
&\sum_{ij}{}' \left\{1 - (\hat{\kappa})_i(\hat{\kappa})_j\right\} \sum_{ts} \kappa_t \kappa_s \left[\frac{(-1)\,(4\pi)\,(2!)\;\langle r_1^2\rangle\langle r_2^4\rangle}{3\; R^3}\right] \sum_m \frac{\left\langle (r_1)_i\; Y_1^{m^*}(1)\right\rangle \left\langle (\hat{r}_2)_t(\hat{r}_2)_s(\hat{r}_2)_j\; Y_{L_2}^{-m^*}(2)\right\rangle}{(1+m)!\,(1-m)!} \\
&= 2\Big\{ \kappa_1\kappa_1 \mathcal{P}_{11} \langle 1\rangle\; \langle 1,1,1\rangle + \kappa_2\kappa_2 \mathcal{P}_{22} \langle 2\rangle\; \langle 2,2,2\rangle + \kappa_3\kappa_3 \mathcal{P}_{33} \langle 3\rangle\; \langle 3,3,3\rangle \\
&\quad + (\kappa_2\kappa_2 \mathcal{P}_{11} + \kappa_1\kappa_1 \mathcal{P}_{22} + 4\,\kappa_1\kappa_2 \mathcal{P}_{12})\; \langle 1\rangle\; \langle 1,2,2\rangle \\
&\quad + (\kappa_3\kappa_3 \mathcal{P}_{11} + \kappa_3\kappa_3 \mathcal{P}_{22} + 2\,\kappa_1\kappa_3 \mathcal{P}_{13} + 2\,\kappa_2\kappa_3 \mathcal{P}_{23})\; \langle 1\rangle\; \langle 1,3,3\rangle \\
&\quad + (\kappa_1\kappa_1 \mathcal{P}_{33} + \kappa_2\kappa_2 \mathcal{P}_{33} + 2\,\kappa_1\kappa_3 \mathcal{P}_{13} + 2\,\kappa_2\kappa_3 \mathcal{P}_{23})\; \langle 3\rangle\; \langle 1,1,3\rangle \Big\} \\
&= -\frac{2\kappa^2}{3}\left[\frac{\langle r_1^2\rangle\langle r_2^4\rangle}{(3)\,(5)\; R^3}\right] (1 - 3\cos^2\theta_\kappa) \quad ;
\end{aligned} \tag{189}$$

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11. The $\hat{\kappa}_i$ denote unit vector components; the parentheses have been left out for convenience.

where θ_κ is defined through $(\hat{\kappa})_3 \equiv \cos\theta_\kappa$, and θ_κ is the angle between $\vec{\kappa}$ and the ζ-axis (Fig. 2). Including this result in equation (181) and incorporating all previous simplifications, yields the following for equation (181):

$$X(3)^{(2)} = -\frac{(2)^3 a^3 X(0)^{(2)}}{(3)^3 (5\pi)} \int_0^\infty b^3 \, db \left[\frac{b}{a(a+b)^2}\right] (3) \left[F(b) + 2\,G(b)\right] . \tag{190}$$

Hence, one obtains the dipole-quadrupole interaction energy due to the mixed terms. This equation is the counter part of equation (147); and by adding these two equations one can obtain the interaction energy correction, accurate to dipole-quadrupole orders, resulting from mixing of the field and electrostatic operators.

The last term in the group being considered is $X(4)^{(2)}$, given by the second set of terms of $X(4)$ in equation (131):

$$\begin{aligned}
X(4)^{(2)} = &\left[-\frac{2\,(E_1-E_0)^4}{2^4\pi^4\hbar^2c^2}\right] \int \kappa\,d\kappa \int \kappa'\,d\kappa' \int d\Omega_\kappa \int d\Omega_{\kappa'} \times \sum_{ij}\sum_{\ell s} \left\{\delta_{ij} - (\hat{\kappa})_i(\hat{\kappa})_s\right\}\left\{\delta_{j\ell} - (\hat{\kappa}')_j(\hat{\kappa}')_\ell\right\} \\
&\left[\left\{\frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{\hbar c(\kappa+\kappa')}\left[\frac{1}{\left[(E_1-E_0)+\hbar c\right]^2}\right.\right.\right. \\
&\qquad \left.\left. + \frac{1}{\left[(E_1-E_0)+\hbar c\kappa\right]\left[(E_1-E_0)+\hbar c\kappa'\right]} \times \left\{1 + \frac{\hbar c(\kappa+\kappa')}{2(E_1-E_0)}\right\}\right]\right\} \\
&\quad \times \left\{-\frac{1}{2}\sum_{tq}\omega_t\,\omega_q\left[\left\langle(\vec{r}_1)_t(\vec{r}_1)_q(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle(\vec{r}_2)_\ell(\vec{r}_2)_s\right\rangle\right.\right. \\
&\qquad \left.\left. + \left\langle(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle(\vec{r}_2)_t(\vec{r}_2)_q(\vec{r}_2)_\ell(\vec{r}_2)_s\right\rangle\right]\right\} \\
&+\left\{\frac{e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1-E_0)+\hbar c\kappa\right]}\left[\frac{1}{2(E_1-E_0)\left[(E_1-E_0)+\hbar c\kappa'\right]} + \frac{1}{\left[2(E_1-E_0)+\hbar c(\kappa+\kappa')\right]}\right.\right. \\
&\qquad \left.\left. \times\left\{\frac{1}{(E_1-E_0)+\hbar c\kappa} + \frac{1}{(E_1-E_0)+\hbar c\kappa'}\right\}\right]\right\} \\
&\quad \times \left\{-\frac{1}{2}\sum_{tq} v_t\,v_q\left[\left\langle(\vec{r}_1)_t(\vec{r}_1)_q(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle(\vec{r}_2)_\ell(\vec{r}_2)_s\right\rangle\right.\right. \\
&\qquad \left.\left.\left. + \left\langle(\vec{r}_1)_i(\vec{r}_1)_j\right\rangle\left\langle(\vec{r}_2)_t(\vec{r}_2)_q(\vec{r}_2)_\ell(\vec{r}_2)_s\right\rangle\right]\right\}\right]
\end{aligned} \tag{191}$$

The evaluation of the preceding factors is accomplished by following the procedure outlined before. The matrix elements of interest are $\left\langle (\vec{r})_i (\vec{r})_j \right\rangle$ and $\left\langle (\vec{r})_i (\vec{r})_j (\vec{r})_t (\vec{r})_s \right\rangle$. These have already been listed in equation (120). The nonzero combinations are:

$$\left\langle (\vec{r})_i (\vec{r})_j \right\rangle = \frac{1}{3} \langle r^2 \rangle \, \delta_{ij} \quad , \qquad i, j = 1, 2, 3,$$

$$\left\langle (\vec{r})_i (\vec{r})_i (\vec{r})_i (\vec{r})_i \right\rangle = \frac{1}{5} \langle r^4 \rangle \quad , \qquad i = 1, 2, 3,$$

$$\left\langle (\vec{r})_1 (\vec{r})_1 (\vec{r})_2 (\vec{r})_2 \right\rangle = \left(\frac{1}{3}\right)\left(\frac{1}{5}\right) \langle r^4 \rangle \quad ,$$

$$\left\langle (\vec{r})_1 (\vec{r})_1 (\vec{r})_3 (\vec{r})_3 \right\rangle = \left(\frac{1}{3}\right)\left(\frac{1}{5}\right) \langle r^4 \rangle \quad ,$$

$$\left\langle (\vec{r})_2 (\vec{r})_2 (\vec{r})_3 (\vec{r})_3 \right\rangle = \left(\frac{1}{3}\right)\left(\frac{1}{5}\right) \langle r^4 \rangle \quad . \tag{192}$$

Defining the expressions containing $\left\{ \delta_{is} - (\hat{\kappa})_i (\hat{\kappa})_s \right\}$ by $\mathcal{P}(i, j, \ell, s)$, one of the sums that needs to be evaluated is given by

$$\sum_{ij} \sum_{\ell s} \mathcal{P}(i, j, \ell, s) \sum_{tq} \omega_t \, \omega_q \left[\left\langle (\vec{r}_1)_t (\vec{r}_1)_q (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \frac{\langle r_2^2 \rangle}{3} \, \delta_{\ell, s} + \frac{\langle r_1^2 \rangle}{3} \, \delta_{ij} \left\langle (\vec{r}_2)_t (\vec{r}_2)_q (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \right] \quad .$$

Since the second factor is obtained by an interchange of r_1 and r_2, only one term needs to be evaluated in detail. Substituting for ω_t, the quantity that needs to be calculated (defining the matrix element as $\langle t, q, i, j \rangle$) is given by

$$\frac{1}{3} \langle r_2^2 \rangle \sum_{ij} \sum_{\ell s} \mathcal{P}(i,j,\ell,s)\ \delta_{\ell s}$$

$$\times \sum_{tq} (\kappa_t \kappa_q + \kappa_t' \kappa_q' + 2\kappa_t \kappa_q')\ \langle t,q,i,j \rangle \quad . \tag{193}$$

By using the results given by equation (192), the factor containing $\kappa_t \kappa_q$ becomes

$$\left(\frac{1}{3}\right)\langle r_2^2\rangle\left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\langle r_1^4\rangle \sum_s \Big\{ \mathcal{P}(1,1,s,s)\ \left[2\kappa_1\kappa_1 + \vec{\kappa}\cdot\vec{\kappa}\right] + \mathcal{P}(2,2,s,s)\ \left[2\kappa_2\kappa_2 + \vec{\kappa}\cdot\vec{\kappa}\right]$$

$$+ \mathcal{P}(3,3,s,s)\ \left[2\kappa_3\kappa_3 + \vec{\kappa}\cdot\vec{\kappa}\right] + \left[\mathcal{P}(1,2,s,s) + \mathcal{P}(2,1,s,s)\right]\left[2\kappa_1\kappa_2\right]$$

$$+ \left[\mathcal{P}(1,3,s,s) + \mathcal{P}(3,1,s,s)\right]\left[2\kappa_1\kappa_3\right]$$

$$+ \left[\mathcal{P}(2,3,s,s) + \mathcal{P}(3,2,s,s)\right]\left[2\kappa_2\kappa_3\right] \Big\} \quad .$$

Using the definition for $\mathcal{P}(i,j,\ell,s)$ and summing over $\underline{s}$, the above result transforms into

$$\left(\frac{1}{3}\right)\langle r_2^2\rangle\left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\langle r_1^4\rangle\ \kappa^2\ \ (1 + \cos^2\Theta) \quad . \tag{194}$$

The term containing $\kappa_t' \kappa_q'$ in equation (193) gives the same result; only κ^2 is replaced by κ'^2. When the last factor that contains $\kappa_t \kappa_q'$ in equation (193) is expanded, it gives the following result:

$$\left(\frac{1}{3}\right)\langle r_2^2\rangle\left(2\right)\left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\langle r_1^4\rangle \sum_s \Big\{ \mathcal{P}(1,1,s,s)\ \left[2\kappa_1\kappa_1' + \vec{\kappa}\cdot\vec{\kappa}'\right]$$

$$+ \mathcal{P}(2,2,s,s)\ \left[2\kappa_2\kappa_2' + \vec{\kappa}\cdot\vec{\kappa}'\right] + \mathcal{P}(3,3,s,s)\ \left[2\kappa_3\kappa_3 + \vec{\kappa}\cdot\vec{\kappa}'\right]$$

$$+ \left[\mathcal{P}(1,2,s,s) + \mathcal{P}(2,1,s,s)\right]\left[\kappa_1\kappa_2' + \kappa_2\kappa_1'\right]$$

$$+ \left[\mathcal{P}(1,3,s,s) + \mathcal{P}(3,1,s,s)\right]\left[\kappa_1\kappa_3' + \kappa_3\kappa_1'\right]$$

$$+ \left[\mathcal{P}(2,3,s,s) + \mathcal{P}(3,2,s,s)\right]\left[\kappa_2\kappa_3' + \kappa_3\kappa_2'\right] \Big\} \ .$$

By using the definitions for $\mathcal{P}(i, j, \ell, s)$ and summing over s, the above expression reduces to

$$\left(\frac{1}{3}\right) \langle r_2^2 \rangle \left(\frac{2}{1}\right)\left(\frac{1}{3}\right) \left(\frac{1}{5}\right) \langle r_1^4 \rangle \, \kappa \, \kappa' \; (2 \cos^3 \Theta) \quad . \tag{195}$$

Collecting these terms, the sums in equation (193) become

$$\frac{\langle r_2^2 \rangle \langle r_1^4 \rangle}{(5)\;(3)^2} \left\{ \left(\kappa^2 + \kappa'^2\right) \; (1 + \cos^2 \Theta) + 4 \, \kappa \, \kappa' \cos^3 \Theta \right\} \quad . \tag{196}$$

Analyzing the expression in equation (193) indicates that when ω_t is replaced by v_t only the sign of $2\,\kappa_t\,\kappa'_q$ changes; hence, only the quantity in equation (195) changes sign. By using these results to evaluate the second term in the sums of equation (191) and performing integrations as before as well as using the results of equation (176), equation (194) reduces to

$$\begin{aligned} X(4)^{(2)} = & - \frac{4\, a^5\, X(0)^{(2)}}{(3)^2\; (5)\; \pi^2} \int b\, db \int \beta\, d\beta \\ & \times \left\{ \frac{(2a + b)}{a(a + b)^2} \left(\frac{1}{b + \beta} + \frac{1}{\beta - b} \right) \right. \\ & \left. + \frac{a(b + \beta) + \beta(a + \beta) + b(a + b)}{a(a + b)\,(a + \beta)\,(b + \beta)\,(b - \beta)} \right\} \\ & \times \left\{ (b^2 + \beta^2) \left[F(b)\; F(\beta) + 2\; G(b)\; G(\beta) \right] \right. \\ & \left. - 2 b \beta \; \frac{\left[\mathcal{F}_2(b)\; \mathcal{F}_2(\beta) + 6\; F_3(b)\; F_3(\beta) \right]}{(b\beta)} \right\} \quad . \end{aligned} \tag{197}$$

The β integrals are evaluated using previous results and values obtained in Appendix C. Since the second fraction containing b and β does not contribute to the integral over β, only the first term needs to be evaluated. To obtain the β integrals in equation (197), one proceeds as follows: Take the first term, given by

$$\int b\,db \int \beta\, d\beta \left[\frac{2a+b}{a(a+b)^2}\right]\left(\frac{1}{b+\beta}+\frac{1}{\beta-b}\right)(b^2+\beta^2)\ \left[F(b)\ F(\beta)+2\ G(b)\ G(\beta)\right]$$

$$= \pi \int_0^\infty \frac{b^3\,db\ (2a+b)}{b^2\ a\ (a+b)^2}\ \left[F(b)+2\ G(b)\right]$$

$$+ 2i\pi \int_0^\infty \frac{b^4\,db\ (2a+b)}{a\ (a+b)^2}\ \left[F(b)\ F^{+}(b)+2\ G(b)\ G^{+}(b)\right] \quad , \qquad (198)$$

and the second integral of equation (197), given by

$$\int b\,db \int \beta\, d\beta \left[\frac{(2a+b)}{a(a+b)^2}\right]\left(\frac{1}{b+\beta}+\frac{1}{\beta-b}\right)\left\{-2\left[\mathcal{F}_2(b)\ \mathcal{F}_2(\beta)+6\ F_3(b)\ F_3(\beta)\right]\right\}$$

$$=\left\{\frac{(8)\,(3\pi)}{2}\int \frac{b\,db}{b^2}\left[\frac{(2a+b)}{a(a+b)^2}\right]\left[\mathcal{F}_2(b)-3\ F_3(b)\right]\right.$$

$$\left.-\frac{(4)\,(i\pi)}{2}\int b^2\,db\left[\frac{2a+b}{a(a+b)^2}\right]\left[\mathcal{F}_2(b)\ \mathcal{F}_2^{-}(b)+6\ F_3(b)\ F_3^{+}(b)\right]\right\} \quad ; \qquad (199)$$

combine these terms and obtain the following expression for equation (197):

$$X(4)^{(2)} = \left[-\frac{4a^5 X(0)^{(2)}}{(3)^3 (5)\pi} \right]$$

$$\times \left[3 \int_0^\infty \frac{b(2a+b)}{a(a+b)^2}\, db \left\{ F(b) + 2\,G(b) + \frac{12}{b^2}\,\mathcal{F}_2(b) - \frac{36}{b^2}\,F_3(b) \right\} \right.$$

$$+ 6i \int_0^\infty \frac{b^4(2a+b)}{a(a+b)^2}\, db \left\{ F(b)\,F^+(b) + 2\,G(b)\,G^+(b) - \frac{\mathcal{F}_2(b)\,\mathcal{F}_2^-(b)}{b^2} \right.$$

$$\left. \left. - \frac{6\,F_3(b)\,F_3^+(b)}{b^2} \right\} \right] \quad . \qquad (200)$$

Further simplification is possible for each of the $X(i)^{(2)}$ terms, by applying the definitions for the various functions used so far. This may be seen by recalling that these functions are defined in terms of $F(b)$ and $G(b)$, used throughout this discussion. For instance $\mathcal{F}_2(b) \equiv b^2\,G(b) - 2\,F_3(b)$, $\mathcal{F}(b) = b^2\,G(b) - F_3(b)$, ... etc.

Dipole-Quadrupole Interaction Energy

In the previous discussion, each of the elements $X(j)^{(2)}$ is given in terms of an integral over $\underline{b}$ $(b = \kappa R)$ and with coefficients proportional to $X(0)^{(2)}$. Combining the expressions in equations (168), (172), (180), (190), and (200), one obtains the dipole-quadrupole order correction to the interaction energy ΔE_{d-q}, given by

$$\Delta E_{d-q} = X(0)^{(2)} \Bigg[1 - \frac{(2)^2 (a)^3}{(3)^3 (5)\pi} \Bigg\{ \Bigg[4 \int b\,db \left\{ (F + 2\,G) + \frac{6}{b^2} (\mathcal{F} - 4\,F_3) \right\}$$

$$+ 8i \int b^4 db \left\{ (F\,F^+ + 2\,G\,G^+) - \frac{1}{b^2} (\mathcal{F}\mathcal{F}^- + 4\,F_3\,F_3^+) \right\} \Bigg]$$

$$- \Bigg[2a \int \frac{b\,db}{(a+b)} \left\{ 5\,(F + 2\,G) + \frac{1}{b^2} \left[12\,\mathcal{F} + 36\,\mathcal{F}_2 - (3)(52)\,F_3 \right] \right\}$$

$$+ 4ai \int \frac{b^4 db}{(a+b)} \left\{ 5\,(F\,F^+ + 2\,G\,G^+) - \frac{1}{b^2} (2\mathcal{F}\mathcal{F}^- + 3\,\mathcal{F}_2\,\mathcal{F}_2^- + 26\,F_3\,F_3^+) \right\} \Bigg]$$

$$+ \Bigg[2 \int \frac{b^4\,b\,d}{a(a+b)^2} \left\{ 3\,(F + 2\,G) \right\} \Bigg]$$

$$+ \Bigg[3a^2 \int \frac{b(2a+b)\,db}{a(a+b)^2} \left\{ (F + 2\,G) + \frac{12}{b^2} (\mathcal{F}_2 - 3\,F_3) \right\}$$

$$+ 6a^2 i \int \frac{b^4 (2a+b)\,db}{a(a+b)^2} \left\{ (F\,F^+ + 2\,G\,G^+) - \frac{1}{b^2} (\mathcal{F}_2\,\mathcal{F}_2^- + 6\,F_3\,F_3^+) \right\} \Bigg] \Bigg\} \Bigg] \quad . \qquad (201)$$

By writing the above equation[12] as a sum of terms, one can see that the result reduces to the electrostatic interaction case when the radiation field is omitted. In addition, each term $X(i)^{(2)}$, $i = 1, 2, 3, 4$, is separated into two integrals over exponentials $e^{\pm i b}$ and $e^{\pm 2 i b}$. The reason for doing this may be seen by referring to the dipole-dipole approximation, where, in equations (162) and (163), one notes that only the integrals over $e^{\pm 2 i b}$ contribute to the final result given in equation (164). The integrals over $e^{\pm i b}$ and portions of the results from the integrals over $e^{\pm 2 i b}$ combine to cancel $X(0)^{(1)}$. One would expect the same behavior for higher approximations, so the results given by equation (200) are already in a suitable form for further analysis.

QUADRUPOLE-QUADRUPOLE APPROXIMATIONS

Introduction

The presentation of the quadrupole-quadrupole order approximations is much more condensed than previous discussions; however, all the steps

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12. In the above expression the explicit functional dependence is omitted.

necessary to obtain a given result are either mentioned explicitly or the intermediate results are given. To have a systematic presentation, the procedure followed here parallels that used in the immediately preceding discussion. The quadrupole-quadrupole order interaction energy is given by

$$\Delta E_{q-q} = X(0)^{(3)} + X(1)^{(3)} + X(2)^{(3)} + X(3)^{(3)} + X(4)^{(3)} \quad , \qquad (202)$$

where the various $X(j)^{(i)}$, $j > 0$, elements are given by the last group of terms in equations (123), (127), (129), and (131). The electrostatic interaction energy $X(0)^{(3)}$ is obtained from equation (85) by letting $L_1 = L_2 = 2$; $M = -2, -1, 0, +1, +2$; and $L_1 = 1$, $L_2 = 3$; $L_1 = 3$, $L_2 = 1$; $M = -1, 0, +1$. Hence substituting these values in equation (85), one obtains

$$X(0)^{(3)} = \Bigg\{ \left[\frac{(-1)^4 \{(4)!\}^2 \langle r_1^4 \rangle \langle r_2^4 \rangle}{2(E_0 - E_1) R^{10} (5)(5)} \right] \sum_{m=-2}^{+2} \frac{1}{(2-m)!\,(2+m)!\,(2-m)!\,(2+m)!}$$

$$+ \left[\frac{(-1)^6 \{(4)!\}^2 \langle r_1^2 \rangle \langle r_2^6 \rangle}{2(E_0 - E_1) R^{10} (3)(7)} + \frac{(-1)^2 \{(4)!\}^2 \langle r_1^6 \rangle \langle r_2^2 \rangle}{2(E_0 - E_1) R^{10} (7)(3)} \right]$$

$$\times \sum_{m=-1}^{+1} \frac{1}{(1-m)!\,(1+m)!\,(3-m)!\,(3+m)!} \Bigg\}$$

$$= \frac{(-1)}{(E_1 - E_0) R^{10}} \left\{ \frac{7}{5} \langle r_1^4 \rangle \langle r_2^4 \rangle + \frac{4}{3} \langle r_1^2 \rangle \langle r_2^6 \rangle \right\} \quad .$$

This result may be expressed in terms of $\langle r_1^4 \rangle \langle r_2^4 \rangle$ by using the following relations, [see equation (86)]:

$$\langle r^6 \rangle = \frac{(2)(7)}{(3)} \langle r^2 \rangle \langle r^4 \rangle \quad , \qquad \langle r^4 \rangle = \frac{(5)}{(2)} \langle r^2 \rangle \langle r^2 \rangle$$

Thus, $X(0)^{(3)}$ may be written as

$$X(0)^{(3)} = - \frac{(5)(7) \langle r_1^4 \rangle \langle r_2^4 \rangle}{3^2 (E_1 - E_0) R^{10}} \quad . \qquad (203)$$

The next term to be evaluated is given by the last group of elements in equation (123):

$$X(1)^{(3)} = \left(-\frac{2\hbar}{2^5 \pi^4 \mu^2 c^3}\right) \int \frac{d\vec{\kappa}}{\kappa} \int \frac{d\vec{\kappa'}}{\kappa'} (1+\cos^2\Theta)\, e^{-i(\vec{\kappa}+\vec{\kappa'})\cdot\vec{R}}$$

$$\times \left[\left(\frac{1}{4}\right)\left(\frac{1}{3}\right)^2 \langle r_1^2\rangle \langle r_2^2\rangle + \left(\frac{1}{24}\right)\left(\frac{1}{5}\right) \left(\langle r_1^4\rangle + \langle r_2^4\rangle\right) \right]$$

$$\times \left\{ (\kappa^2 + \kappa'^2) + 4\,\kappa\,\kappa'\,(\kappa^2+\kappa'^2)\cos\Theta + 4\,\kappa^2\,\kappa'^2\cos^2\Theta \right\} \quad . \tag{204}$$

The coefficient of this term may be expressed in terms of $\langle r_1^4\rangle\langle r_2^4\rangle$ by using the relations previously obtained. Combining the $\underline{r}$ matrix elements, and substituting for $(1/2\mu c^2)$, one obtains

$$\left[-\frac{(E_1 - E_0)^2 \langle r_1^4\rangle\langle r_2^4\rangle}{(2)^3 (3)^4 (\pi)^4 (5) (\hbar c)^3} \right] \quad .$$

Again substituting for κ and κ' and using the above coefficient, as well as expressing the quantities in terms of $\underline{a}$ and $X(0)^{(3)}$, equation (204) becomes

$$X(1)^{(3)} = \left[\frac{2^2 a^3 X(0)^{(3)}}{(7)(3)^2(5)^2\pi^2} \right] \int b\,db \int \frac{\beta\,d\beta}{(b+\beta)}$$

$$\times \Bigg\{ (b^2+\beta^2)^2 \left[F(b)\,F(\beta) + 2\,G(b)\,G(\beta)\right]$$

$$- 2b\beta\,(b^2+\beta^2)\,\frac{\left[\mathcal{F}(b)\,\mathcal{F}(\beta) + 4\,F_3(b)\,F_3(\beta)\right]}{b\beta}$$

$$+ b^2\beta^2 \Bigg[\left\{F_2(b)\,F_2(\beta) + 2\,G(b)\,G(\beta)\right\}$$

$$+ \frac{1}{b^2\beta^2}\left\{ f(b)\,f(\beta) + 12\,\mathcal{F}_4(b)\,\mathcal{F}_4(\beta) + 24\,F_3(b)\,F_3(\beta)\right\} \Bigg] \Bigg\} \quad , \tag{205}$$

where

$$F_2(b) = F(b) + G(b)\,, \quad f(b) = b^2\, F_4(b) - 8\, F_3(b)\,, \quad \mathcal{F}_4(b) = b^2\, G(b) - 4\, F_3(b) \quad .$$

The β integrals are performed with the aid of Appendix C. The results for each of the above integrals are as follows, (after the β integrations, the explicit functional dependence is omitted):

$$\int b\, db \int \beta\, d\beta \left(\frac{1}{b+\beta} \right) (b^2 + \beta^2)^2 \left[F(b)\; F(\beta) + 2\, G(b)\; G(\beta) \right]$$

$$= \pi \int_0^\infty b^3\, db \left\{ F + 2\, G \right\} + 4\, i\, \pi \int_0^\infty b^6\, db \left\{ F\, F^+ + 2\, G\, G^+ \right\} \qquad ,$$

$$\int b\, db \int \beta\, d\beta \left(\frac{1}{b+\beta} \right) \left[b\beta\; (b^2 + \beta^2) \right] \left[\frac{\mathcal{F}(b)\; \mathcal{F}(\beta) + 4\, F_3(b)\; F_3(\beta)}{b\beta} \right]$$

$$= -\,3\pi \int_0^\infty b\, db \left\{ \mathcal{F} - 4\, F_3 \right\} + i\pi \int_0^\infty b^4\, db \left\{ \mathcal{F}\mathcal{F}^- + 4\, F_3\, F_3^+ \right\} \qquad ,$$

$$\int b\, db \int \frac{\beta\, d\beta\, (b^2 \beta^2)}{(b+\beta)} \left\{ \left[F_2(b)\; F_2(\beta) + 2\, G(b)\; G(\beta) \right] \right.$$

$$\left. + \frac{1}{b^2 \beta^2} \left[f(b)\; f(\beta) + 12\, \mathcal{F}_4(b)\; \mathcal{F}_4(\beta) + 24\, F_3(b)\; F_3(\beta) \right] \right\}$$

$$= -\,24\,\pi \int_0^\infty \frac{db}{b} \left\{ f + 6\, \mathcal{F}_4 - 3\, F_3 \right\} + i\pi \int_0^\infty b^2\, db \left\{ b^4\, F_2\, F_2^+ + 2\, b^4\, G\, G^+ \right.$$

$$\left. + f\, f^+ + 12\, \mathcal{F}_4\, \mathcal{F}_4^- + 24\, F_3\, F_3^+ \right\} \, .$$

Using the above integrals, the expression in equation (205) becomes

$$X(1)^{(3)} = \left[\frac{2^2 a^3 X(0)^{(3)}}{(7)(3)^2(5)^2 \pi} \right]$$

$$\times \left\{ \int_0^\infty db \left[b^3(F + 2G) + 12b(\mathcal{F} - 4F_3) - \frac{48}{b}(f + 6\mathcal{F}_4 - 3F_3) \right] \right.$$

$$+ 4i \int_0^\infty db \left[b^6 (F F^+ + 2 G G^+) - b^4 (\mathcal{F}\mathcal{F}^- + 4 F_3 F_3^+) \right.$$

$$+ \frac{b^6}{2} (F_2 F_2^+ + 2 G G^+)$$

$$\left. \left. + \frac{b^2}{2} (f f^- + 12 \mathcal{F}_4 \mathcal{F}_4^- + 24 F_3 F_3^+) \right] \right\} \quad . \qquad (206)$$

In the above expression, the explicit functional dependence in the various functions has been omitted. This will be done in the future after doing the β integrations. Comparison of equation (206) to the expression for $X(1)^{(2)}$ given in equation (172) shows the increased complexity in the higher approximations, even for $X(1)^{(i)}$ which is the simplest of the electromagnetic interaction terms.

The next term to be considered is obtained from the last group of elements in equation (127); it is given by

$$X(2)^{(3)} = \left[-\frac{2(E_1 - E_0)^2}{2^4 \pi^4 \mu c^3 \hbar} \right] \int \frac{d\vec{\kappa}}{\kappa} \int \frac{d\vec{\kappa}'}{\kappa'} \sum_{ij} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j - (\hat{\kappa}')_i (\hat{\kappa}')_j + (\hat{\kappa})_i (\hat{\kappa}')_j (\hat{\kappa}\cdot\hat{\kappa}') \right\}$$

$$\times \left\{ \left[\frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa+\kappa')\left[(E_1 - E_0) + \hbar c \kappa\right]} + \frac{e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{(\kappa+\kappa')\left[(E_1 - E_0) + \hbar c \kappa'\right]} \right] \right.$$

$$\times \left[\frac{1}{4} \sum_{ts} \sum_{qh} \left\{ \left(\frac{1}{6}\right)\left(\frac{1}{3}\right) \left\langle r_2^2 \right\rangle \delta_{ij}\, \omega_t \omega_s \omega_q \omega_h \left\langle (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_q (\vec{r}_1)_h \right\rangle \right. \right.$$

$$+ \left(\frac{1}{3}\right) \left\langle r_1^2 \right\rangle \omega_t \omega_s \delta_{ts} \omega_q \omega_h \left\langle (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle$$

$$\left. \left. + \left(\frac{1}{6}\right) \omega_t \omega_s \omega_q \omega_h \left\langle (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle \right\} \right]$$

$$+\left[\frac{\hbar c\, e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c\kappa\right]\left[(E_1 - E_0) + \hbar c\kappa'\right]}\right]$$

$$\times\left[\frac{1}{4}\sum_{ts}\sum_{qh}\left\{\left(\frac{1}{6}\right)\left(\frac{1}{3}\right)\left\langle r_2^2\right\rangle \delta_{ij}\, v_t\, v_s\, v_q\, v_h \left\langle (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_q (\vec{r}_1)_h \right\rangle\right.\right.$$

$$+ \left(\frac{1}{3}\right)\left\langle r_1^2\right\rangle v_t\, v_s\, \delta_{ts}\, v_q\, v_h \left\langle (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle$$

$$\left.\left.+ \left(\frac{1}{6}\right) v_t\, v_s\, v_q\, v_h \left\langle (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle\right\}\right]\Bigg\} \quad . \tag{207}$$

To evaluate the terms in equation (207), one needs to consider three different types of sums, as given in the above expression. Since the evaluation of these sums is very involved, only the intermediate results are given in each case. Denoting the sums over unit vectors $(\hat{\kappa})_i$ by $\mathcal{P}(i, j)$, the first sum to be considered is

$$\left(\frac{1}{24}\right)\left(\frac{\langle r_2^2\rangle}{3}\right)\sum_{ij}\mathcal{P}(i,j)\sum_{ts}\sum_{qh}\delta_{ij}\,\omega_t\,\omega_s\,\omega_q\,\omega_h\left\langle (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_q (\vec{r}_1)_h\right\rangle \quad .$$

Using the matrix values for $\left\langle (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_q (\vec{r}_1)_h\right\rangle$ obtained before, the expansion over t, s, q, and h is simplified considerably. Furthermore, the δ_{ij} function allows one to collapse the sum over i, j. After this is done, the above sum reduces to

$$\left(\frac{1}{24}\right)\left(\frac{\langle r_2^2\rangle}{3}\right)\left(\frac{1}{3}\right)\left(\frac{1}{5}\langle r_1^4\rangle\right)(3)\left[(\kappa^2 + \kappa'^2) + 4\,\kappa\,\kappa'\,(\kappa^2 + \kappa'^2)\cos\Theta\right.$$

$$\left. + 4\,\kappa^2\,\kappa'^2\cos^2\Theta\right](1 + \cos^2\Theta) \quad . \tag{208}$$

The next sum to be evaluated is

$$\left(\frac{1}{4}\right)\left(\frac{\langle r_1^2\rangle}{3}\right)\sum_{ij}\mathcal{P}(i,j)\sum_{ts}\sum_{qh}\omega_t\,\omega_s\,\delta_{t,s}\,\omega_q\,\omega_h\left\langle (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle \quad .$$

Summing over $\underline{t}$, first, and then over i, j, q, h, the above expression becomes

$$\frac{\langle r_1^2 \rangle}{(4)(3)} \left[\sum_s (\kappa_s + \kappa_s')^2 \right] \left[\frac{\langle r_2^4 \rangle}{(3)(5)} \right] \left[(\kappa^2 + \kappa'^2)(1 + \cos^2 \Theta) + 4 \kappa \kappa' \cos^3 \Theta \right]$$

$$= \frac{\langle r_1^2 \rangle \langle r_2^4 \rangle}{(4)(3)(3)(5)} \left[(\kappa^2 + \kappa'^2)^2 (1 + \cos^2 \Theta) + 2 \kappa \kappa' (\kappa^2 + \kappa'^2)(\cos \Theta + 3 \cos^3 \Theta) \right.$$

$$\left. + 8 \kappa^2 \kappa'^2 \cos^4 \Theta \right] \quad . \tag{209}$$

Evaluation of the last sum in equation (207), given by

$$\left(\frac{1}{24} \right) \sum_{ij} \mathcal{P}(i,j) \sum_{ts} \sum_{qh} \omega_t \omega_s \omega_q \omega_h \left\langle (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_i (\vec{r}_2)_j \right\rangle ,$$

is carried out by first replacing ω and ω' with κ and κ' in the above expression, and then performing the multiplications indicated. Five different sets of $(\kappa)_i$, $(\kappa')_j$ combinations are obtained; for instance, one of these sets having no primed components is $(\kappa_t \kappa_s \kappa_q \kappa_h)$. The other groups have various combinations of (κ_t) and (κ_t'). The matrix elements over $(\vec{r})_i$ are evaluated in the same manner as those for dipole-quadrupole approximations; the nonzero combinations are as follows:

$$\left\langle (\vec{r})_i (\vec{r})_i (\vec{r})_i (\vec{r})_i (\vec{r})_i (\vec{r})_i \right\rangle = \frac{\langle r^6 \rangle}{7} , \quad i = 1, 2, 3 \quad ,$$

$$\left\langle (\vec{r})_i (\vec{r})_i (\vec{r})_i (\vec{r})_i (\vec{r})_j (\vec{r})_j \right\rangle = \frac{\langle r^6 \rangle}{(5)(7)} , \quad i, j = 1, 2, 3; \; i \neq j \quad ,$$

$$\left\langle (\vec{r})_i (\vec{r})_i (\vec{r})_j (\vec{r})_j (\vec{r})_t (\vec{r})_t \right\rangle = \frac{\langle r^6 \rangle}{(3)(5)(7)} , \quad i, j, t, = 1, 2, 3; \; i \neq j \neq t \quad . \tag{210}$$

Using these results, the term being considered reduces to

$$\left(\frac{1}{24}\right) \sum_{ij} \mathcal{P}(i,j) \sum_{ts} \sum_{qh} \langle t, s, q, h, i, j \rangle$$

$$\times \left\{ \kappa_t \kappa_s \kappa_q \kappa_h + \kappa'_t \kappa'_s \kappa'_q \kappa'_h + 6\, \kappa_t \kappa_s \kappa'_q \kappa'_h + 4\, \kappa_t \kappa_s \kappa_q \kappa'_h + 4\, \kappa_t \kappa'_s \kappa'_q \kappa'_h \right\}$$

$$= \frac{\langle r^6 \rangle}{(8)(3)(5)(7)} \left\{ (\kappa^2 + \kappa'^2)^2 (1 + \cos^2 \Theta) + 4\, \kappa^2 \kappa'^2 \, (-\cos^2 \Theta + 3 \cos^4 \Theta) \right.$$

$$\left. + 8\, \kappa \kappa' \, (\kappa^2 + \kappa'^2) \cos^3 \Theta \right\} \quad . \qquad (211)$$

Analysis of equation (211) shows that when the sums containing (v_i) in equation (207) are evaluated, a sign change occurs in those terms containing $\cos \Theta$ or $\cos^3 \Theta$. Thus, using previous results, one notes that the two groups of terms in equation (207) combine after the integrations over $d\Omega$ are performed because of a sign change introduced in these terms in these operations. [See equation (176).] Thus, the equivalent of equation (207) may be written as

$$X(2)^{(3)} = \left[\frac{2\,(E_1 - E_0)^2}{2^4 \pi^4 \mu c^3 \hbar} \right] \int \kappa \, d\kappa \int \kappa' d\kappa' \int d\Omega_\kappa \int d\Omega_{\kappa'} \, e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot \vec{R}}$$

$$\times \left\{ \frac{1}{(\kappa + \kappa')\left[(E_1 - E_0) + \hbar c \kappa\right]} + \frac{1}{(\kappa + \kappa')\left[(E_1 - E_0) + \hbar c \kappa'\right]} \right.$$

$$\left. + \frac{\hbar c}{\left[(E_1 - E_0) + \hbar c \kappa\right]\left[(E_1 - E_0) + \hbar c \kappa'\right]} \right\}$$

$$\times \left\{ \left[\frac{\langle r_2^2 \rangle \langle r_1^4 \rangle}{(24)(3)(5)} \right] \left\{ \left[(\kappa^2 + \kappa'^2)^2 + 4\, \kappa \kappa' \, (\kappa^2 + \kappa'^2) \cos \Theta + 4\, \kappa' \kappa'^2 \cos^2 \Theta \right] \times (1 + \cos^2 \Theta) \right\} \right.$$

$$+ \left(\frac{1}{4}\right) \left[\frac{\langle r_1^2 \rangle \langle r_2^4 \rangle}{(3)(3)(5)} \right] \left[(\kappa^2 + \kappa'^2)^2 (1 + \cos^2 \Theta) + 2\, \kappa \kappa' \, (\kappa^2 + \kappa'^2)(\cos \Theta + 3 \cos^3 \Theta) \right.$$

$$\left. + 8\, \kappa^2 \kappa'^2 \cos^4 \Theta \right]$$

$$+ \frac{\langle r^6 \rangle}{(8)(3)(5)(7)} \left[(\kappa^2 + \kappa'^2)^2 (1 + \cos^2 \Theta) + 4\, \kappa^2 \kappa'^2 \, (-\cos^2 \Theta + 3 \cos^4 \Theta) \right.$$

$$\left. \left. + 8\, \kappa \kappa' \, (\kappa^2 + \kappa'^2) \cos^3 \Theta \right] \right\} \quad ,$$

where one combines the terms in equation (207) before the integrations over $d\Omega$ are performed. An additional simplification to equation (207) is accomplished by expressing (μ) in terms of $\langle r^2 \rangle$ and the resulting factors in terms of $\langle r_1^4 \rangle \langle r_2^4 \rangle$. After performing these modifications, expressing κ and κ' in terms of b and β, and listing the coefficient in terms of $\underline{a}$ and $X(0)^{(3)}$, the preceding equation becomes

$$X(2)^{(3)} = -\frac{a^4 X(0)^{(3)}}{2^4 \pi^4 (3)(5)^3(7)} \int_0^\infty b\,db \int_0^\infty \beta\,d\beta \int d\Omega_\kappa \int d\Omega_{\kappa'}\, e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}$$

$$\times \left\{ \frac{1}{b+\beta}\left(\frac{1}{a+b} + \frac{1}{a+\beta}\right) + \frac{1}{(a+b)(a+\beta)} \right\}$$

$$\times \left\{ 5(b^2+\beta^2)^2 (1+\cos^2\Theta) + 8b\beta(b^2+\beta^2)(\cos\Theta + 4\cos^3\Theta) \right.$$

$$\left. - 4b^2\beta^2(\cos^2\Theta - 11\cos^4\Theta) \right\} \quad . \tag{212}$$

By performing the integrations over $d\Omega$ the above expression simplifies to

$$X(2)^{(3)} = -\frac{2^2 a^4 X(0)^{(3)}}{(3)(7)(5)^3 \pi^2} \int_0^\infty b\,db \int_0^\infty \frac{\beta\,d\beta}{(a+b)} \left[\frac{1}{(b+\beta)} + \frac{1}{(\beta-b)} + \frac{b(a+b)+\beta(a+\beta)}{(b-\beta)(b+\beta)(a+\beta)} \right]$$

$$\times \left\{ 5(b^2+\beta^2)^2 \left[F(b)\,F(\beta) + 2\,G(b)\,G(\beta)\right] \right.$$

$$- 4b\beta(b^2+\beta^2)\left[bG(b)\,\beta G(\beta) + 4\frac{\left[\mathcal{F}_2(b)\,\mathcal{F}_2(\beta) + 6\,F_3(b)\,F_3(\beta)\right]}{b\beta} \right]$$

$$\left. - 2b^2\beta^2 \left[F_2(b)\,F_2(\beta) + 2\,G(b)\,G(\beta) - 11\frac{\left[f(b)\,f(\beta) + 12\,\mathcal{F}_4(b)\,\mathcal{F}_4(\beta) + 24\,F_3(b)\,F_3(\beta)\right]}{b^2\beta^2} \right] \right\}. \tag{213}$$

Since the second fraction involving b and β does not contribute to the β integral, one needs only consider the following β integrals:

$$\int b\,db \int \beta\,d\beta \left(\frac{1}{a+b}\right)\left(\frac{1}{b+\beta}+\frac{1}{\beta-b}\right)(b^2+\beta^2)^2 \left[F(b)\,F(\beta)+2\,G(b)\,G(\beta)\right]$$

$$= \pi \int_0^\infty \frac{b^3\,db}{(a+b)} \{F+2\,G\} + 4\,i\,\pi \int_0^\infty \frac{b^6\,db}{(a+b)} \{F\,F^+ + 2\,G\,G^+\} \quad ,$$

$$\int_0^\infty b\,db \int_0^\infty \beta\,d\beta \left(\frac{1}{a+b}\right)\left(\frac{1}{b+\beta}+\frac{1}{\beta-b}\right)\left[b\beta(b^2+\beta^2)\right] \times \left\{ b\,G(b)\,\beta\,G(\beta) + \frac{4\,\mathcal{F}_2(b)\,\mathcal{F}_2(\beta)+24\,F_3(b)\,F_3(\beta)}{b\,\beta} \right\}$$

$$= -(8)(3\pi) \int_0^\infty \frac{b\,db}{(a+b)} \{\mathcal{F}_2 - 3\,F_3\} + 2\,\pi\,i \int_0^\infty \frac{b^8\,db}{(a+b)} \left\{ G\,G^+ + \frac{4\,\mathcal{F}_2\,\mathcal{F}_2^-}{b^4} + \frac{24\,F_3\,F_3^+}{b^4} \right\} \quad ,$$

$$\int_0^\infty b\,db \int_0^\infty \beta\,d\beta \left[\frac{1}{(a+b)}\right]\left(\frac{1}{b+\beta}+\frac{1}{\beta-b}\right)\Big\{ b^2\beta^2 \left[F_2(b)\,F_2(\beta)+2\,G(b)\,G(\beta)\right]$$

$$- 11\left[f(b)\,f(\beta) + 12\,\mathcal{F}_4(b)\,\mathcal{F}_4(\beta) + 24\,F_3(b)\,F_3(\beta)\right]\Big\}$$

$$= (2)(11)(12)\,\pi \int_0^\infty \frac{db}{b(a+b)} \{f + 6\,\mathcal{F}_4 - 3\,F_3\} + i\,\pi \int_0^\infty \frac{b^6\,db}{(a+b)} \Big\{ (F_2\,F_2^+ + 2\,G\,G^+)$$

$$- \frac{11}{b^4}(f\,f^- + 12\,\mathcal{F}_4\,\mathcal{F}_4^- + 24\,F_3\,F_3^+) \Big\} \quad .$$

Incorporating these results into equation (213), one gets

$$X(2)^{(3)} = -\frac{(2)^2\,a^4\,X(0)^{(3)}}{(3)\,(5)^3(7)\,(\pi)}$$

$$\times \Bigg[\int_0^\infty \frac{db}{(a+b)} \Big\{ 5\,b^3\,(F+2\,G) + (4)(8)(3)\,b\,(\mathcal{F}_2 - 3\,F_3)$$

$$- \frac{(2)(2)(11)(12)}{b}(f + 6\,\mathcal{F}_4 - 3\,F_3)\Big\}$$

$$+ i \int_0^\infty \frac{b^6\,db}{(a+b)} \Big\{ (5)(4)\,(F\,F^+ + 2\,G\,G^+)$$

$$- (4)(2)\left(b^2\,G\,G^+ + \frac{4\,\mathcal{F}_2\,\mathcal{F}_2^-}{b^2} + \frac{24\,F_3\,F_3^+}{b^2}\right)$$

$$- 2\Big(\left[F_2\,F_2^+ + 2\,G\,G^+\right]$$

$$- \frac{11}{b^4}\left[f\,f^- + 12\,\mathcal{F}_4\,\mathcal{F}_4^- + 24\,F_3\,F_3^+\right]\Big)\Big\}\Bigg] \quad . \qquad (214)$$

Using the definitions for the various functions, one notes that the preceding result is separated into two terms proportional to $e^{\pm ib}$ and $e^{\pm 2ib}$, as done previously.

The next term to be evaluated is $X(3)^{(3)}$. This term consists of the last group of elements in equation (129) and the terms of quadrupole-quadrupole order in the second group of this equation. [See equations (182) and (183).] The reasons for including all these terms here were explained in the preceding discussion. Collecting these terms, $X(3)^{(3)}$ is given by

$$X(3)^{(3)} = \left[-\frac{4\,(E_1 - E_0)^2}{2^3 \pi^2 \hbar c} \right] \int \kappa\, d\kappa \int d\Omega_\kappa \sum_{ij} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j \right\} e^{-i\vec{\kappa}\cdot\vec{R}}$$

$$\times \left\{ \frac{1}{(E_1 - E_0)\left[(E_1 - E_0) + \hbar c \kappa\right]} + \frac{-1}{\left[(E_1 - E_0) + \hbar c\kappa\right]^2} \right\}$$

$$\times \left\{ \sum_{ts} \kappa_t \kappa_s \left[\left\langle H_q^{(2)}\, (\vec{r}_1)_t (\vec{r}_1)_i (\vec{r}_2)_s (\vec{r}_2)_j \right\rangle - \left\langle H_q^{(2)}\, (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle \right] \right.$$

$$+ \frac{1}{24} \sum_{ts} \sum_{lh} \kappa_t \kappa_s \kappa_l \kappa_h$$

$$\times \left[\left\langle H_q^{(2)}\, (\vec{r}_1)_i (\vec{r}_2)_t (\vec{r}_2)_s (\vec{r}_2)_l (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle - 4 \left\langle H_q^{(2)}\, (\vec{r}_1)_t (\vec{r}_1)_i (\vec{r}_2)_s (\vec{r}_2)_l (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle \right.$$

$$+ 6 \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_i (\vec{r}_2)_l (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle - 4 \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_l (\vec{r}_1)_i (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle$$

$$\left.\left. + \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_l (\vec{r}_1)_h (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle \right] \right\} . \tag{215}$$

Expressing the elements involving $(\hat{\kappa})_i$ as $\mathcal{P}_{ij}$, the sums needed in the above equation are evaluated as follows: The first term to be considered gives[13]

13. Using equation (183) one picks out only the terms for which $L_1 = L_2 = 2$.

$$\sum_{ij} \mathcal{P}_{ij} \sum_{ts} \kappa_t \kappa_s \left\langle H_q^{(2)} \; (\vec{r}_1)_t (\vec{r}_1)_i (\vec{r}_2)_s (\vec{r}_2)_j \right\rangle$$

$$= \sum_{ij} \mathcal{P}_{ij} \sum_{ts} \left[\frac{(-1)^2 (4\pi)(4!)}{5\, R^5} \right] \langle r_1^4 \rangle \langle r_2^4 \rangle$$

$$\times \sum_{m=-2}^{+2} \left[\frac{1}{(2-m)!\,(2+m)!} \right] \left\langle (\hat{r}_1)_i (\hat{r}_1)_t \, Y_2^{m*} (1) \right\rangle \left\langle (\hat{r}_2)_j (\hat{r}_2)_s \, Y_2^{-m*} (2) \right\rangle$$

$$= - \frac{4\kappa^2 \langle r_1^4 \rangle \langle r_2^4 \rangle}{(3)(4)(5)^2 R^5} \left\{ 3 - 30 \cos^2 \theta_\kappa + 35 \cos^4 \theta_\kappa \right\} \quad , \qquad (216)$$

where the following nonzero matrix elements have been used:

$$\left\langle H_q^{(2)} (\vec{r})_i (\vec{r})_i (\vec{r})_i (\vec{r})_i \right\rangle = \left(\frac{3}{12} \right) \left(\frac{4 \langle r_1^4 \rangle \langle r_2^4 \rangle}{5^2 \, R^5} \right) \quad , \quad i = 1, 2 \quad ,$$

$$\left\langle H_q^{(2)} (\vec{r})_i (\vec{r})_i (\vec{r})_i (\vec{r})_i \right\rangle = \left(\frac{8}{12} \right) \left(\frac{4 \langle r_1^4 \rangle \langle r_2^4 \rangle}{5^2 \, R^5} \right) \quad , \quad i = 3 \quad ,$$

$$\left\langle H_q^{(2)} (\vec{r})_i (\vec{r})_j (\vec{r})_i (\vec{r})_j \right\rangle = \left(\frac{1}{12} \right) \left(\frac{4 \langle r_1^4 \rangle \langle r_2^4 \rangle}{5^2 \, R^5} \right) \quad , \quad i, j = 1, 2, \quad i \neq j \quad ,$$

$$\left\langle H_q^{(2)} (\vec{r})_i (\vec{r})_i (\vec{r})_j (\vec{r})_j \right\rangle = \left(\frac{1}{12} \right) \left(\frac{4 \langle r_1^4 \rangle \langle r_2^4 \rangle}{5^2 \, R^5} \right) \quad , \quad i, j = 1, 2, \quad i \neq j \quad ,$$

$$\left\langle H_q^{(2)} (\vec{r})_i (\vec{r})_j (\vec{r})_i (\vec{r})_j \right\rangle = \left(-\frac{4}{12} \right) \left(\frac{4 \langle r_1^4 \rangle \langle r_2^4 \rangle}{5^2 \, R^5} \right) \quad , \quad i, j = 1, 3, \quad i \neq j \quad ,$$

$$\left\langle H_q^{(2)} (\vec{r})_i (\vec{r})_i (\vec{r})_j (\vec{r})_j \right\rangle = \left(-\frac{4}{12} \right) \left(\frac{4 \langle r_1^2 \rangle \langle r_2^4 \rangle}{5^2 \, R^5} \right) \quad , \quad i, j = 1, 3, \quad i \neq j \quad ,$$

$$\left\langle H_q^{(2)} (\vec{r})_i (\vec{r})_j (\vec{r})_i (\vec{r})_j \right\rangle = \left(-\frac{4}{12}\right)\left(\frac{4\langle r_1^2\rangle\langle r_2^4\rangle}{5^2 R^5}\right) , \quad i, j = 2, 3, \quad i \neq j ,$$

$$\left\langle H_q^{(2)} (\vec{r})_i (\vec{r})_i (\vec{r})_j (\vec{r})_j \right\rangle = \left(-\frac{4}{12}\right)\left(\frac{4\langle r_1^2\rangle\langle r_2^4\rangle}{5^2 R^5}\right) , \quad i, j = 2, 3, \quad i \neq j ,$$

(217)

The remainder of the matrix elements are obtained by interchanging t and i in $(\vec{r}_1)$ and j and s in $(\vec{r}_2)$. Recall that the evaluation of each element in equation (217) follows the same path as that followed to obtain equation (187).

The next sum to be evaluated gives

$$- \sum_{ij} \mathcal{P}_{ij} \sum_{ts} \kappa_t \kappa_s \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle$$

$$= - \sum_{ij} \mathcal{P}_{ij} \sum_{ts} \kappa_t \kappa_s \left[\frac{(-1)^1 (4\pi)(4)! \ \langle r_1^6\rangle\langle r_2^2\rangle}{[(3)(7)]^{1/2}} \right]$$

$$\times \sum_{m=-1}^{+1} \frac{\left\langle (\hat{r}_1)_t (\hat{r}_1)_s (\hat{r}_1)_i \, Y_3^{m^*}(1) \right\rangle \left\langle (\hat{r}_2)_j \, Y_1^{-m^*}(2) \right\rangle}{\left\{ (1+m)!\,(1-m)!\,(3+m)!\,(3-m)! \right\}^{1/2}} \quad . \tag{218}$$

The above results are obtained by taking $L_1 = 3$, $L_2 = 1$ in the expression for $H_q^{(2)}$. The choice of L values is made using the results of equation (185). The various matrix products needed to evaluate equation (218), [defining quantities as in equation (188)] are:

$$\langle 1,1,1\rangle \ \langle 1\rangle = -1 \, \frac{\langle r_1^6\rangle\langle r_2^2\rangle}{(5)(7) R^5} = \langle 2,2,2\rangle \ \langle 2\rangle ,$$

$$\langle 1,2,2\rangle \ \langle 1\rangle = -\frac{1}{3} \, \frac{\langle r_1^6\rangle\langle r_2^2\rangle}{(5)(7) R^5} = \langle 1,2,2\rangle \ \langle 2\rangle ,$$

$$\langle 1,3,3\rangle \ \langle 1\rangle = \frac{4}{3} \, \frac{\langle r_1^6\rangle\langle r_2^2\rangle}{(5)(7) R^5} = \langle 2,3,3\rangle \ \langle 2\rangle ,$$

$$\langle 3,3,3\rangle \langle 3\rangle = -\frac{8}{3} \frac{\langle r_1^6\rangle \langle r_2^2\rangle}{(5)(7)R^5} ,$$

$$\langle 1,1,3\rangle \langle 3\rangle = \frac{4}{3} \frac{\langle r_1^6\rangle \langle r_2^2\rangle}{(5)(7)R^5} = \langle 2,2,3\rangle \langle 3\rangle . \tag{219}$$

Using these results equation (218) becomes

$$- \sum_{i,j} \mathcal{P}_{ij} \sum_{t,s} \kappa_t \kappa_s \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_i (\vec{r}_2)_j \right\rangle$$

$$= -\frac{\kappa^2}{3} \left[\frac{\langle r_1^2\rangle \langle r_2^6\rangle}{(3)(7)R^5} \right] (1 - 36 \cos^2\theta_\kappa + 23 \cos^4\theta_\kappa) ,$$

$$= -\frac{4\kappa^2 \langle r_1^4\rangle \langle r_2^4\rangle}{(3)^2(5)^2 R^5} \left\{ 1 - 36 \cos^2\theta_\kappa + 23 \cos^4\theta_\kappa \right\} , \tag{220}$$

where the last step is obtained by substituting for $\langle r^6\rangle$ and $\langle r^2\rangle$ in terms of $\langle r^4\rangle$.

The next sum to be considered is given by

$$\sum_{ij} \mathcal{P}_{ij} \left(\frac{1}{24}\right) \sum_{ts} \sum_{qh} \kappa_t \kappa_s \kappa_q \kappa_h (6) \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_i (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle$$

$$= \frac{1}{4} \sum_{ij} \mathcal{P}_{ij} \sum_{ts} \sum_{qh} \kappa_t \kappa_s \kappa_q \kappa_h \sum_{L_1, L_2} \frac{(-1)^{L_2} (4\pi) (L_1 + L_2)! \left\langle r_1^{L_1+3}\right\rangle \left\langle r_2^{L_2+3}\right\rangle}{R^{L_1+L_2+1} \left\{ (2L_1+1)(2L_2+1) \right\}^{1/2}}$$

$$\times \sum_m \frac{\left\langle (\hat{r}_1)_t (\hat{r}_1)_s (\hat{r}_1)_i Y_{L_1}^{m*}(1) \right\rangle \left\langle (\hat{r}_2)_q (\hat{r}_2)_h (\hat{r}_2)_j Y_{L_2}^{-m*}(2) \right\rangle}{\left\{ (L_1+m)!(L_1-m)!(L_2-m)!(L_2+m)! \right\}^{1/2}} . \tag{221}$$

The matrix elements required to evaluate the above sum have been evaluated and are listed in equation (220). The quadrupole-quadrupole order terms are obtained by choosing only the terms for which $L_1 = L_2 = 1$ in equation (221). Letting

$$\left\langle H_q^{(2)} \, (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_i (\vec{r}_2)_l (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle \equiv \langle t, s, i \rangle \langle l, h, j \rangle \quad ,$$

the nonzero matrix products corresponding to equation (221) are as follows:

$$\begin{aligned}
\langle 1,1,1\rangle \langle 1,1,1\rangle &= \left(\frac{3}{5}\right)\left(\frac{\langle r_1^4\rangle\langle r_2^4\rangle}{(3)(5)\,R^3}\right) = \langle 2,2,2\rangle \langle 2,2,2\rangle \quad , \\
\langle 1,1,1\rangle \langle 1,2,2\rangle &= \left(\frac{1}{5}\right)\left(\frac{\langle r_1^4\rangle\langle r_2^4\rangle}{(3)(5)\,R^3}\right) = \langle 1,1,1\rangle \langle 1,3,3\rangle \quad , \\
\langle 1,2,2\rangle \langle 1,2,2\rangle &= \left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\left(\frac{\langle r_1^4\rangle\langle r_2^4\rangle}{(3)(5)\,R^3}\right) = \langle 1,2,2\rangle \langle 1,3,3\rangle \quad , \\
\langle 1,1,3\rangle \langle 1,1,3\rangle &= \left(-\frac{2}{3}\right)\left(\frac{1}{5}\right)\left(\frac{\langle r_1^4\rangle\langle r_2^4\rangle}{(3)(5)\,R^3}\right) = \langle 1,1,3\rangle \langle 2,2,3\rangle \quad , \\
\langle 2,2,2\rangle \langle 1,1,2\rangle &= \left(\frac{1}{5}\right)\left(\frac{\langle r_1^4\rangle\langle r_2^4\rangle}{(3)(5)\,R^3}\right) = \langle 2,2,2\rangle \langle 2,3,3\rangle \quad , \\
\langle 1,3,3\rangle \langle 1,3,3\rangle &= \left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\left(\frac{\langle r_1^4\rangle\langle r_2^4\rangle}{(3)(5)\,R^3}\right) = \langle 2,3,3\rangle \langle 2,3,3\rangle \quad , \\
\langle 3,3,3\rangle \langle 3,3,3\rangle &= \left(-\frac{6}{5}\right)\left(\frac{\langle r_1^4\rangle\langle r_2^4\rangle}{(3)(5)\,R^3}\right) \quad , \\
\langle 3,3,3\rangle \langle 1,1,3\rangle &= \left(-\frac{2}{5}\right)\left(\frac{\langle r_1^4\rangle\langle r_2^4\rangle}{(3)(5)\,R^3}\right) = \langle 3,3,3\rangle \langle 2,2,3\rangle \quad , \\
\langle 2,2,3\rangle \langle 2,2,3\rangle &= \left(-\frac{2}{3}\right)\left(\frac{1}{5}\right)\left(\frac{\langle r_1^4\rangle\langle r_2^4\rangle}{(3)(5)\,R^3}\right) \quad , \\
\langle 1,1,2\rangle \langle 1,1,2\rangle &= \left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\left(\frac{\langle r_1^4\rangle\langle r_2^4\rangle}{(3)(5)\,R^3}\right) = \langle 1,1,2\rangle \langle 2,3,3\rangle \quad .
\end{aligned} \tag{222}$$

Using these results, the sums in equation (221) are evaluated and the results are given by

$$\left(\frac{1}{4}\right) \sum_{ij} \mathcal{P}_{ij} \sum_{ts} \sum_{lh} \kappa_t \kappa_s \kappa_q \kappa_h \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_s (\vec{r}_1)_i (\vec{r}_2)_l (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle$$

$$= -\frac{\kappa^4 \langle r_1^4 \rangle \langle r_2^4 \rangle}{(4)(3)^2(5)^2 R^3} \left(1 - 3\cos^2\theta_\kappa\right) \quad . \tag{223}$$

This result is in itself interesting, in that after numerous operations on the terms in the sums, the final result can be expressed in terms of $(\hat{\kappa})_3(\hat{\kappa})_3 = \cos^2\theta_\kappa$. In the evaluation of $X(3)^{(3)}$ the angle θ_κ plays the same role as Θ in the terms having both κ and κ'.

The next sum to be evaluated is

$$-\left(\frac{4}{24}\right) \sum_{ij} \mathcal{P}_{ij} \sum_{ts} \sum_{lh} \kappa_t \kappa_s \kappa_l \kappa_h \left\langle H_q^{(2)} (\vec{r}_1)_t (\vec{r}_1)_i (\vec{r}_2)_s (\vec{r}_2)_l (\vec{r}_2)_h (\vec{r}_2)_j \right\rangle \quad .$$

The sum obtained from this expression by replacing $(\vec{r}_1)$ and $(\vec{r}_2)$ has the same value and need not be evaluated. Substituting for $H_q^{(2)}$ in this expression, one finds that matrix elements of the form

$$\left\langle (\hat{r}_1)_t (\hat{r}_1)_i Y_{L_1}^{m*}(1) \right\rangle \quad \text{and} \quad \left\langle (\hat{r}_2)_s (\hat{r}_2)_l (\hat{r}_2)_h (\hat{r}_2)_j Y_{L_2}^{-m*}(2) \right\rangle \quad ,$$

need to be evaluated. The former group has already been evaluated and is listed in equation (183). This group of terms requires that $L_1 = 2$ for nonzero results. Thus, the quadrupole-quadrupole order terms associated with this sum require that $L_2 = 0$ to get results proportional to $\langle r_1^4 \rangle \langle r_2^4 \rangle$. With these restrictions, one notes that sums of this type do not contribute to the quadrupole-quadrupole order results.

The last two sums that need to be evaluated are of the form $\frac{1}{24}\sum_{ij}\mathcal{P}_{ij}\sum_{ts}\sum_{lh}\kappa_t\kappa_s\kappa_q\kappa_h\left\langle H_q^{(2)}(\vec{r})_i(\vec{r})_t(\vec{r})_s(\vec{r})_l(\vec{r})_h(\vec{r})_j\right\rangle$, the other being obtained by interchanging $(\vec{r_1})$ and $(\vec{r_2})$. Substituting for $H_q^{(2)}$ in terms of r_1 and r_2, one notes that matrix elements of the form $\left\langle(\vec{r_1})_i Y_{L_1}^{m*}(1)\right\rangle$ and $\left\langle(\vec{r_2})_t(\vec{r_2})_s(\vec{r_2})_l(\vec{r_2})_h(\vec{r_2})_j Y_{L_2}^{-m*}(2)\right\rangle$ need to be considered. The former set is given by equation (143), where one sees that only the value $L_1 = 1$ gives nonzero results. To quadrupole-quadrupole orders, then, L_2 can be only unity. Hence, this sum reduces to

$$\left(\frac{1}{24}\right)\sum_{ij}\mathcal{P}_{ij}\sum_{ts}\sum_{lh}\kappa_t\kappa_s\kappa_q\kappa_h\left\langle H_q^{(2)}(\vec{r_1})_i(\vec{r_2})_t(\vec{r_2})_s(\vec{r_2})_l(\vec{r_2})_h(\vec{r_2})_j\right\rangle$$

$$=\left(\frac{1}{24}\right)\left[\frac{(-1)(4\pi)(2!)\langle r_1^2\rangle\langle r_2^6\rangle}{3R^3}\right]\sum_{ij}\mathcal{P}_{ij}\sum_{ts}\sum_{qh}\kappa_t\kappa_s\kappa_q\kappa_h$$

$$\times\sum_{m=-1}^{+1}\frac{\left\langle(\hat{r}_1)_i Y_1^{m*}(1)\right\rangle\left\langle(\hat{r}_2)_t(\hat{r}_2)_s(\hat{r}_2)_q(\hat{r}_2)_h(\hat{r}_2)_j Y_1^{-m*}(2)\right\rangle}{(1-m)!(1+m)!}\ . \tag{224}$$

The matrix elements in this equation are evaluated in the same manner as before; except now, the substitution of the $(\vec{r})_i$ components requires the use of up to fifth-order Spherical Harmonics. These functions may be obtained using the definitions for $Y_L^m(\theta,\phi)$ given in equation (21). The nonzero matrix products corresponding to equation (224) are as follows:

$$\langle 1\rangle\ \langle 1,1,1,1,1\rangle = (1)\left(\frac{\langle r_1^2\rangle\langle r_2^6\rangle}{(3)(7)R^3}\right) = \langle 2\rangle\ \langle 2,2,2,2,2\rangle\ ,$$

$$\langle 1\rangle\ \langle 1,1,1,2,2\rangle = \left(\frac{1}{5}\right)\left(\frac{\langle r_1^2\rangle\langle r_2^6\rangle}{(3)(7)R^3}\right) = \langle 1\rangle\ \langle 1,1,1,3,3\rangle\ ,$$

$$\langle 1\rangle\ \langle 1,2,2,2,2\rangle = \left(\frac{1}{5}\right)\left(\frac{\langle r_1^2\rangle\langle r_2^6\rangle}{(3)(7)\ R^3}\right) = \langle 1\rangle\ \langle 1,3,3,3,3\rangle \quad ,$$

$$\langle 1\rangle\ \langle 1,2,2,3,3\rangle = \left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\left(\frac{\langle r_1^2\rangle\langle r_2^6\rangle}{(3)(7)\ R^3}\right) = \langle 2\rangle\ \langle 1,1,2,3,3\rangle \quad ,$$

$$\langle 2\rangle\ \langle 1,1,1,1,2\rangle = \left(\frac{1}{5}\right)\left(\frac{\langle r_1^2\rangle\langle r_2^6\rangle}{(3)(7)\ R^3}\right) = \langle 2\rangle\ \langle 2,3,3,3,3\rangle \quad ,$$

$$\langle 2\rangle\ \langle 1,1,2,2,2\rangle = \left(\frac{1}{5}\right)\left(\frac{\langle r_1^2\rangle\langle r_2^6\rangle}{(3)(7)\ R^3}\right) = \langle 2\rangle\ \langle 2,2,2,3,3\rangle \quad ,$$

$$\langle 3\rangle\ \langle 3,3,3,3,3\rangle = (-2)\left(\frac{\langle r_1^2\rangle\langle r_2^6\rangle}{(3)(7)\ R^3}\right) \quad ,$$

$$\langle 3\rangle\ \langle 1,1,1,1,3\rangle = \left(-\frac{2}{5}\right)\left(\frac{\langle r_1^2\rangle\langle r_2^6\rangle}{(3)(7)\ R^3}\right) = \langle 3\rangle\ \langle 2,2,2,2,3\rangle \quad ,$$

$$\langle 3\rangle\ \langle 1,1,3,3,3\rangle = \left(-\frac{2}{5}\right)\left(\frac{\langle r_1^2\rangle\langle r_2^6\rangle}{(3)(7)\ R^3}\right) = \langle 3\rangle\ \langle 2,2,3,3,3\rangle \quad ,$$

$$\langle 3\rangle\ \langle 1,1,2,2,3\rangle = \left(\frac{1}{3}\right)\left(-\frac{2}{5}\right)\left(\frac{\langle r_1^2\rangle\langle r_2^6\rangle}{(3)(7)\ R^3}\right) \quad . \tag{225}$$

Using these results, the sums in equation (224) combine to give

$$\left(\frac{1}{24}\right)\sum_{ij}\mathcal{P}_{ij}\sum_{ts}\sum_{lh}\kappa_t\,\kappa_s\,\kappa_q\,\kappa_h\left\langle H_q^{(2)}\,(\vec{r}_1)_i(\vec{r}_2)_t(\vec{r}_2)_s(\vec{r}_2)_l\,(\vec{r}_2)_h(\vec{r}_2)_j\right\rangle$$

$$= -\frac{4\,\langle r_1^4\rangle\langle r_2^4\rangle\kappa^4}{(24)(3)^2(5)^2\,R^3}\left\{1 + 9\cos^2\theta_\kappa - 12\cos^4\theta_\kappa\right\} \quad , \tag{226}$$

where the last results is obtained by replacing $\langle r^6\rangle\langle r^2\rangle$ in terms of $\langle r^4\rangle\langle r^4\rangle$. The sum obtained by interchanging $(\vec{r}_1)$ and $(\vec{r}_2)$ in equation (224) is the same as in equation (226). Substituting these results in equation (215), letting $\kappa R = b$, and factoring common factors, this equation becomes

$$X(3)^{(3)} = \left[-\frac{4\,(E_1 - E_0)^2}{2^3 \pi^2 (\hbar c)^3} \right] \left[-\frac{\langle r_1^4 \rangle \langle r_2^4 \rangle}{(2)^2 (3)^3 (5)^2} \right]$$

$$\times \int b\,db \int d\Omega_\kappa \, e^{-i \vec{\kappa} \cdot \vec{R}} \left\{ \frac{1}{a(a+b)} + \frac{-1}{(a+b)^2} \right\}$$

$$\times \Big\{ (2)^2 (3)^2 b^2 \left[3 - 30 \cos^2 \theta_\kappa + 35 \cos^4 \theta_\kappa \right]$$

$$+ (3)(4)^2 b^2 \left[1 - 36 \cos^2 \theta_\kappa + 23 \cos^4 \theta_\kappa \right] + 3b^4 \left[1 - 3 \cos^2 \theta_\kappa \right]$$

$$+ (2)^2 b^4 \left[1 + 9 \cos^2 \theta_\kappa - 12 \cos^4 \theta_\kappa \right] \Big\}$$

$$= -\frac{a^3 X(0)^{(3)}}{(7)(2)^3 (3)(5)^3 \pi^2} \int b\,db \left[\frac{b}{a(a+b)^2} \right]$$

$$\times \int d\Omega_\kappa \, e^{-i b \cos \theta_\kappa} \Big\{ (3)(2)^2 b^2 \left[13 - 234 \cos^2 \theta_\kappa + 197 \cos^4 \theta_\kappa \right]$$

$$+ b^4 \left[7 + 27 \cos^2 \theta_\kappa - 48 \cos^4 \theta_\kappa \right] \Big\} \quad . \quad (227)$$

Using the results of Appendix B to perform the integrations over $d\Omega$, the above integrals reduce to

$$\int d\Omega_\kappa \, e^{-i b \cos \theta_\kappa} \left[13 - 234 \cos^2 \theta_\kappa + 197 \cos^4 \theta_\kappa \right]$$

$$= \int d\Omega_\kappa \, e^{-i b \cos \theta_\kappa} \left[13(1 - 3 \cos^2 \theta_\kappa) - 195 (\cos^2 \theta_\kappa - \cos^4 \theta_\kappa) + 2 \cos^4 \theta_\kappa \right]$$

$$= \left\{ (13)(-2^3 \pi)(F_3) + (195)(2^3 \pi) \left(\frac{\mathcal{F}_4}{b^2} \right) + (2) \frac{\left[4\pi f(b) \right]}{b^2} \right\} \quad ,$$

$$\int d\Omega_\kappa \, e^{-ib\cos\theta_\kappa} \left[7 + 27\cos^2\theta_\kappa - 48\cos^4\theta_\kappa\right]$$

$$= \left\{ (7)(-2^3\pi)(F_3) - (48)(2^3\pi)\frac{\mathcal{F}_4}{b^2} \right\} \quad .$$

Using the above results, equation (227) becomes

$$X(3)^{(3)} = \frac{a^3 X(0)^{(3)}}{(7)(3)(5)^3\pi} \int \frac{b^2\,db}{a(a+b)^2}$$

$$\times \left\{ (3)(2)^2 b^2 \left[(13) F_3 - 195\frac{\mathcal{F}_4}{b^2} - \frac{f(b)}{b^2} \right] + b^4 \left[7 F_3 + 48 \frac{\mathcal{F}_4}{b^2} \right] \right\} \quad . \tag{228}$$

The last term to be evaluated is given by the last group of terms in equation (218), and is given here by

$$X(4)^{(3)} = \left[-\frac{2(E_1 - E_0)^4}{2^4\pi^4\hbar^2c^2} \right] \int \kappa\,d\kappa \int \kappa' d\kappa' \int d\Omega_\kappa \int d\Omega_{\kappa'}$$

$$\times \sum_{ij}\sum_{\ell s} \left\{ \delta_{is} - (\hat{\kappa})_i(\hat{\kappa})_s \right\} \left\{ \delta_{j\ell} - (\hat{\kappa}')_j(\hat{\kappa}')_\ell \right\}$$

$$\times \left[\frac{e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}}{\hbar c(\kappa+\kappa')} \left\{ \frac{1}{\left[(E_1 - E_0) + \hbar c\kappa\right]^2} + \frac{2(E_1 - E_0) + \hbar c(\kappa+\kappa')}{\left[(E_1 - E_0) + \hbar c\right]\left[(E_1 - E_0) + \hbar c\kappa'\right]\left[2(E_1 - E_0)\right]} \right\} \right.$$

$$\times \left\{ \frac{1}{24} \sum_{tq}\sum_{hf} \omega_t\omega_q\omega_h\omega_f \left[\left\langle (\vec{r}_1)_t(\vec{r}_1)_q(\vec{r}_1)_h(\vec{r}_1)_f(\vec{r}_1)_i(\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_\ell(\vec{r}_2)_s \right\rangle \right.\right.$$

$$+ 6 \left\langle (\vec{r}_1)_t(\vec{r}_1)_q(\vec{r}_1)_i(\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_h(\vec{r}_2)_f(\vec{r}_2)_\ell(\vec{r}_2)_s \right\rangle$$

$$\left.\left. + \left\langle (\vec{r}_1)_i(\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_t(\vec{r}_2)_q(\vec{r}_2)_h(\vec{r}_2)_f(\vec{r}_2)_\ell(\vec{r}_2)_s \right\rangle \right] \right\}$$

$$+ \frac{e^{-i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}}}{\left[(E_1 - E_0) + \hbar c\kappa\right]} \left\{ \frac{1}{2(E_1 - E_0)\left[(E_1 - E_0) + \hbar c\kappa'\right]} \right.$$

$$+ \frac{2(E_1 - E_0) + \hbar c(\kappa+\kappa')}{\left[2(E_1 - E_0) + \hbar c(\kappa+\kappa')\right]\left[(E_1 - E_0) + \hbar c\kappa\right]\left[(E_1 - E_0) + \hbar c\kappa'\right]}$$

$$\times \left\{ \frac{1}{24} \sum_{tq} \sum_{hf} v_t v_q v_h v_f \left[\left\langle (\vec{r}_1)_t (\vec{r}_1)_q (\vec{r}_1)_h (\vec{r}_1)_f (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \right.\right.$$

$$+ 6 \left\langle (\vec{r}_1)_t (\vec{r}_1)_q (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_h (\vec{r}_2)_f (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle$$

$$\left.\left. + \left\langle (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_t (\vec{r}_2)_q (\vec{r}_2)_h (\vec{r}_2)_f (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \right] \right\} \Bigg] \; . \tag{229}$$

The evaluation of this equation requires evaluation of six different sums involving ω_i and v_i. Later on, one will see that it is necessary to do only the sums involving ω_i. Taking the first sum, given by

$$\sum_{ij} \sum_{\ell s} \mathcal{P}(i,j,\ell,s) \left(\frac{1}{24}\right) \sum_{tq} \sum_{hf} \omega_t \omega_q \omega_h \omega_f \left\langle (\vec{r}_1)_t (\vec{r}_1)_q (\vec{r}_1)_h (\vec{r}_1)_f (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle ,$$

one evaluates it by using the results of equations (120) and (210), where the various matrix elements needed have already been listed. The results are as follows:

$$\left(\frac{1}{24}\right)\left(\frac{1}{3}\right) \langle r_2^2 \rangle \left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\left(\frac{1}{7}\right) \langle r_1^6 \rangle \Big\{ (3)\,(\kappa^4 + \kappa'^4)\,(1 + \cos^2 \Theta)$$

$$+ 6\,(\kappa^2 \kappa'^2)\,(1 - \cos^2 \Theta + 6 \cos^4 \Theta)$$

$$+ (4)\,(3)\,(2)\,(\kappa^3 \kappa' + \kappa'^3 \kappa) \cos^3 \Theta \Big\} . \tag{230}$$

The listing of terms reflects the expansion of $(\omega_t \omega_q \omega_h \omega_f)$ into various $(\kappa)_i$ and $(\kappa')_j$ components, as was explicitly indicated in equation (211). The sum obtained by interchanging $(\vec{r}_1)$ and $(\vec{r}_2)$ yields the same results and need not be evaluated. The next sum to be evaluated is given by

$$\sum_{i,j} \sum_{\ell,s} \mathcal{P}(i,j,\ell,s) \left(\frac{1}{24}\right) \sum_{t,q} \sum_{hf} \omega_t \omega_q \omega_h \omega_f \left[6 \left\langle (\vec{r}_1)_t (\vec{r}_1)_q (\vec{r}_1)_i (\vec{r}_1)_j \right\rangle \left\langle (\vec{r}_2)_h (\vec{r}_2)_f (\vec{r}_2)_\ell (\vec{r}_2)_s \right\rangle \right] .$$

The evaluation of this term is accomplished using the results given in equation (175) for the matrix elements. Since t, q, h, and f appear in different matrix elements, one must be careful when performing the expansions and contractions of the various $(\kappa)_i$ and $(\kappa')_j$ components. In addition, since $i, j, \ell,$ and s are coupled in both matrix elements and the polarization function $\mathcal{P}(i, j, \ell, s)$, the sums are not straightforward. Applying the various techniques developed in evaluating previous sums of this type, one finally obtains the following result for this sum:

$$
\begin{aligned}
\left(\frac{1}{4}\right)\left(\frac{1}{3}\right)\left(\frac{1}{5}\right) \langle r_1^4 \rangle \left(\frac{1}{3}\right)\left(\frac{1}{5}\right) \langle r_2^4 \rangle \Big\{ & (\kappa^4 + \kappa'^4)(1 + \cos^2\Theta) \\
& + 2\,\kappa^2\,\kappa'^2\,(1 + \cos^2\Theta) \\
& + 4\,\kappa^2\,\kappa'^2\,(1 - 3\cos^2\Theta + 4\cos^4\Theta) \\
& + 4\,(\kappa^3\kappa' + \kappa'^3\kappa)\,(2\cos^3\Theta) \Big\} \quad .
\end{aligned}
\tag{231}
$$

Analysis of the results in equations (230) and (231) shows that, when the next group of sums in equation (229), containing (v_t) instead of (ω_t) is evaluated, the elements undergoing a sign change correspond to terms containing $\cos^3\Theta$. This property allows one to combine the two groups of terms in equation (229) because the integrations over $d\Omega$ of $\cos\Theta$ and $\cos^3\Theta$ give an additional sign change which offsets the previous variation in sign of the terms in question. It is of interest to note that while this feature of the calculations appears throughout the various approximations considered, it is necessary to keep the various terms separated until the final sums and integrations over $d\Omega$ are carried out. In all previous cases this has been done, except in equation (212), where the various terms in equation (207) were combined before performing the integrations over $d\Omega$. This will also be done here to shorten the discussion. Hence, incorporating the results given in equations (230) and (231), and combining the various elements in equation (229), one obtains

$$X(4)^{(3)} = \left[-\frac{2(E_1 - E_0)^4}{2^4 \pi^4 \hbar^2 c^2} \right] \int \frac{b\,db}{R^2} \int \frac{\beta\,d\beta}{R^2} \int d\Omega_\kappa \int d\Omega_{\kappa'}\, e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}$$

$$\times \left\{ \frac{R^3}{(\hbar c)^3 (b+\beta)} \left[\frac{1}{(a+b)^2} + \frac{2a + (b+\beta)}{2a(a+b)(a+\beta)} \right] \right.$$

$$\left. + \frac{R^3}{(\hbar c)^3 (a+b)} \left[\frac{1}{2a(a+b)} + \frac{2a + (b+\beta)}{(2a+b+\beta)(a+b)(a+\beta)} \right] \right\}$$

$$\times \left\{ \frac{2 \langle r_2^2 \rangle \langle r_1^6 \rangle (3)}{(24)(3)^2(5)(7) R^4} \left[(b^4 + \beta^4)(1 + \cos^2\Theta + 2b^2\beta^2)(1 - \cos^2\Theta + 6\cos^4\Theta) \right. \right.$$

$$\left. + 8(b^3\beta + \beta^3 b)\cos^3\Theta \right]$$

$$+ \frac{\langle r_1^4 \rangle \langle r_2^4 \rangle}{(4)(3)^2(5)^2 R^4} \left[(b^4 + \beta^4)(1 + \cos^2\Theta) \right.$$

$$+ 2b^2\beta^2(1 + \cos^2\Theta) + 4b^2\beta^2(1 - 3\cos^2\Theta + 4\cos^4\Theta)$$

$$\left. \left. + 8(b^3\beta + \beta^3 b)\cos^3\Theta \right] \right\} . \tag{232}$$

Expressing $\langle r^2 \rangle$ and $\langle r^6 \rangle$ in terms of $\langle r^4 \rangle$ and rearranging terms, equation (232) becomes

$$X(4)^{(3)} = \frac{\left[-2(E_1 - E_0)^4 \right]}{2^4 \pi^4 (\hbar c)^5 R^5} \cdot \frac{\langle r^4 \rangle \langle r^4 \rangle}{(4)(3)^3(5)^2} \int b\,db \int \beta\,d\beta\, e^{-i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}$$

$$\times \left\{ \frac{(2a+b)}{a(a+b)^2} \left(\frac{1}{b+\beta} + \frac{1}{\beta - b} \right) + \frac{a(b+\beta) + \beta(a+\beta) + b(a+b)}{a(a+b)(a+\beta)(b+\beta)(b-\beta)} \right\}$$

$$\times \left\{ 7(b^4 + \beta^4)(1 + \cos^2\Theta) \right.$$

$$+ 2b^2\beta^2(13 - 19\cos^2\Theta + 48\cos^4\Theta)$$

$$\left. + 8(b^3\beta + \beta^3 b)(7\cos^3\Theta) \right\} .$$

Expressing the coefficient in terms of $\underline{a}$ and $X(0)^{(3)}$, and performing the integrations over $d\Omega$, the preceding expression becomes

$$
\begin{aligned}
X(4)^{(3)} = &\left[\frac{a^5\, X(0)^{(3)}}{(7)\,(3)\,(\pi)^2\,(5)^3} \right] \\
&\times \int b\,db \int \beta\, d\beta \left\{ \frac{(2a+b)}{a(a+b)^2} \left(\frac{1}{b+\beta} + \frac{1}{\beta - b} \right) \right. \\
&\qquad \left. + \frac{a(b+\beta) + \beta(a+\beta) + b(a+b)}{a(a+b)\,(a+\beta)\,(b+\beta)\,(b-\beta)} \right\} \\
&\times \left\{ 7(b^4+\beta^4)\,\left[F(b)\;F(\beta) + 2\,G(b)\;G(\beta)\right] \right. \\
&\quad + 2b^2\beta^2 \left[\frac{13}{2} \left\{F(b) - G(b)\right\} \left\{F(\beta) - G(\beta)\right\} \right. \\
&\qquad - \frac{19}{2} \left\{F_2(b)\;F_2(\beta) + 2\,G(b)\;G(\beta)\right\} \\
&\qquad \left. + \frac{48}{2} \;\frac{\left\{f(b)\;f(\beta) + 12\,\mathcal{F}_4(b)\;\mathcal{F}_4(\beta) + 24\,F_3(b)\;F_3(\beta)\right\}}{b^2\beta^2} \right] \\
&\quad \left. - 8\,(b^3\beta + \beta^3 b) \left[\frac{7}{2} \;\frac{\left[\mathcal{F}_2(b)\;\mathcal{F}_2(\beta) + 6\,F_3(b)\;F_3(\beta)\right]}{b\beta} \right] \right\}. \qquad (233)
\end{aligned}
$$

The integrations over β are executed using the following results:

$$\int \frac{b(2a+b)\,db}{a(a+b)^2} \int \frac{2\beta^2\,d\beta}{(\beta+b)(\beta-b)} (b^4+\beta^4) \left[F(b)\,F(\beta) + 2\,G(b)\,G(\beta)\right]$$

$$= \pi \int_0^\infty \frac{b^3(2a+b)\,db}{a(a+b)^2} \left\{F + 2G\right\} + 2i\pi \int_0^\infty \frac{b^6(2a+b)\,db}{a(a+b)^2} \left\{F\,F^+ + 2\,G\,G^+\right\} \quad ,$$

$$\int \frac{b(2a+b)\,db}{a(a+b)^2} \int \frac{2\beta^2\,d\beta}{(\beta+b)(\beta-b)} (b^2\beta^2) \left[\left\{F(b) - G(b)\right\}\left\{F(\beta) - G(\beta)\right\}\right]$$

$$= i\pi \int_0^\infty \frac{b^6(2a+b)\,db}{a(a+b)^2} (F-G)(F^+ - G^+) \quad ,$$

$$\int \frac{b(2a+b)\,db}{a(a+b)^2} \int \frac{2\beta^2\,d\beta}{(\beta+b)(\beta-b)} (b^2\beta^2) \left[F_2(b)\,F_2(\beta) + 2\,G(b)\,G(\beta)\right]$$

$$= i\pi \int_0^\infty \frac{b^6(2a+b)\,db}{a(a+b)^2} \left\{F_2\,F_2^+ + 2\,G\,G^+\right\} \quad ,$$

$$\int \frac{b(2a+b)\,db}{a(a+b)^2} \int \frac{2\beta^2\,d\beta}{(\beta+b)(\beta-b)} (b^2\beta^2) \left[\frac{f(b)\,f(\beta) + 12\,\mathcal{F}_4(b)\,\mathcal{F}_4(\beta) + 24\,F_3(b)\,F_3(\beta)}{b^2\beta^2}\right]$$

$$= -24\pi \int_0^\infty \frac{(2a+b)\,db}{ab(a+b)^2} \left\{f + 6\,\mathcal{F}_4 - 3\,F_3\right\} + i\pi \int_0^\infty \frac{b^2(2a+b)\,db}{a(a+b)^2} \left\{f\,f^- + 12\,\mathcal{F}_4\,\mathcal{F}_4^- + 24\,F_3\,F_3^+\right\} \quad ,$$

$$\int \frac{b(2a+b)\,db}{a(a+b)^2} \int \frac{2\beta^2\,d\beta}{(\beta+b)(\beta-b)} (b^3\beta + \beta^3 b) \left[\frac{\mathcal{F}_2(b)\,\mathcal{F}_2(\beta) + 6\,F_3(b)\,F_3(\beta)}{b\beta}\right]$$

$$= -6\pi \int_0^\infty \frac{b(2a+b)\,db}{a(a+b)^2} \left\{\mathcal{F}_2 - 3\,F_3\right\} + 2i\pi \int_0^\infty \frac{b^4(2a+b)\,db}{a(a+b)^2} \left\{\mathcal{F}_2\,\mathcal{F}_2^- + 6\,F_3\,F_3^+\right\} \quad .$$

Using the above integrals, equation (233) becomes

$$\begin{aligned}
X(4)^{(3)} = & \left[\frac{a^5\,X(0)^{(3)}}{(7)(3)(5)^3\pi}\right] \\
& \times \Bigg\{ \int_0^\infty \frac{(2a+b)\,db}{a(a+b)^2} \Bigg[7b^3(F + 2G) - \frac{(48)(24)}{b}(f + 6\,\mathcal{F}_4 - 3\,F_3) \\
& \qquad + (4)(7)(6)\,b\,(\mathcal{F}_2 - 3\,F_3)\Bigg] \\
& + i \int_0^\infty \frac{b^6(2a+b)\,db}{a(a+b)^2} \Bigg[(2)(7)(F\,F^+ + 2\,G\,G^+) + 13\,(F-G)(F^+ - G^+) \\
& \qquad - (19)(F_2\,F_2^+ + 2\,G\,G^+) - \frac{(7)(8)}{b^2}(\mathcal{F}_2\,\mathcal{F}_2^- + 6\,F_3\,F_3^+) \\
& \qquad + \frac{(48)}{b^4}(f\,f^- + 12\,\mathcal{F}_4\,\mathcal{F}_4^- + 24\,F_3\,F_3^+)\Bigg]\Bigg\} \quad .
\end{aligned} \tag{234}$$

The preceding result for $X(4)^{(3)}$ may be expressed in terms of polynomials in $\underline{b}$ and exponential functions $e^{\pm ib}$ and $e^{\pm 2ib}$ by using the definitions for $F(b)$, $G(b)$, ... $f(b)$, given throughout the discussion. If this is done, the resulting expression would cover several pages; therefore, this will not be done here.

Quadrupole-Quadrupole Interaction Energy

Having evaluated each of the $X(j)^{(3)}$ quantities in equation (202), the expression for the quadrupole-quadrupole order correction to the interaction energy may be written down using the quantities defined in equations (203), (206), (214), (228), and (234). By referring to each one of these equations, one can see that each of the terms $X(j)^{(3)}$, $j \neq 0$, has been given as sums of two terms proportional to $e^{\pm ib}$ and $e^{\pm 2ib}$ and that each coefficient has been expressed in terms of $X(0)^{(3)}$. Hence, substituting for the various $X(j)^{(3)}$, equation (202) becomes

$$
\begin{aligned}
\Delta E_{q-q} = X(0)^{(3)} \Bigg[1 + \frac{a^3}{(3)(5)^3 7\pi} \Bigg\{ \frac{20}{3} \Bigg[\int_0^\infty db \left\{ b^3 (F + 2G) + 12b(\mathcal{F} - 4F_3) - \frac{48}{b}(f + 6\mathcal{F}_4 - 3F_3) \right\} \\
+ 4i \int_0^\infty db \Big\{ b^6 (F F^+ + 2 G G^+) + \frac{b^6}{2}(F_2 F_2^+ + 2 G G^+) \\
- b^4 (\mathcal{F}\mathcal{F}^- + 4 F_3 F_3^+) + \frac{b^2}{2}(f f^- + 12 \mathcal{F}_4 \mathcal{F}_4^- + 24 F_3 F_3^+) \Big\} \Bigg] \\
- 4a \Bigg[\int_0^\infty \frac{db}{(a+b)} \Big\{ 5b^3 (F + 2G) + (4)(8)(3)\, b\, (\mathcal{F}_2 - 3F_3) \\
- \frac{(2)(2)(11)(12)}{b}(f + 6\mathcal{F}_4 - 3F_3) \Big\} \\
+ i \int_0^\infty \frac{db}{(a+b)} \Big\{ (5)(4)\, b^6 (F F^+ + 2 G G^+) - 2b^6 (F_2 F_2^+ + 2 G G^+) \\
- (4)(2)\, b^4 (b^4 G G^+ + 4 \mathcal{F}_2 \mathcal{F}_2^- + 24 F_3 F_3^+) \\
+ (2)(11)\, b^2 (f f^- + 12 \mathcal{F}_4 \mathcal{F}_4^- + 24 F_3 F_3^+) \Big\} \Bigg] \\
+ \Bigg[\int_0^\infty \frac{b^2 db}{a(a+b)^2} \left\{ 12 b^2 \left[13 F_3 - (13)(15)\frac{\mathcal{F}_4}{b^2} - \frac{f(b)}{b^2} \right] + b^4 \left(7 F_3 + \frac{48 \mathcal{F}_4}{b^2} \right) \right\} \Bigg]
\end{aligned}
$$

$$
+ a^2 \left[\int_0^\infty \frac{(2a + b)\,db}{a(a+b)^2} \left\{ 7b^3 (F + 2G) - \frac{(48)(24)}{b} (f + 6 \mathcal{F}_4 - 3 F_3) \right. \right.
$$

$$
\left. + (4)(7)(6)\, b\, (\mathcal{F}_2 - 3 F_3) \right\}
$$

$$
+ i \int_0^\infty \frac{(2a + b)\,db}{a(a+b)^2} \left\{ (2)(7)\, b^6 (F F^+ + 2 G G^+) \right.
$$

$$
+ 13\, b^6 (F - G)(F^+ - G^+) - 19\, b^6 (F_2 F_2^+ + 2 G G^+)
$$

$$
- 56\, b^4 (\mathcal{F}_2 \mathcal{F}_2^- + 6 F_3 F_3)
$$

$$
\left. \left. \left. + 48\, b^2 (f f^- + 12 \mathcal{F}_4 \mathcal{F}_4^- + 24 F_3 F_3^+) \right\} \right] \right\} \Bigg] \quad . \tag{235}
$$

In the above expression for $\Delta E_{q\text{-}q}$, various groups of functions appear in more than one place and each group of terms consists of two integral expressions proportional to $e^{\pm i b}$ and $e^{\pm 2 i b}$ as before. Comparison of equations (201) and (235) shows explicitly the increased complexity encountered in going from the dipole-quadrupole to quadrupole-quadrupole approximations. In particular, the group of terms corresponding to $X(3)^{(3)}$ is much larger than the corresponding group in $X(3)^{(2)}$. This shows that if one is interested in the coupling between $H_q^{(2)}$ and the field operators for approximations beyond the dipole-dipole, one must go on to quadrupole-quadrupole orders before obtaining additional results of interest.

ADDITIONAL RESULTS AND CONCLUSIONS

General Remarks

In this calculation the interaction energy of a two-atom system has been obtained to quadrupole-quadrupole orders. The results are given in terms of the various approximations, to compare the first order results with those of Casimir and Polder [1]. Subsequent approximations are expressed in terms of the electrostatic interaction energy $X(0)^{(i)}$, which in turn gives self-consistent results in the various degrees of approximation. This procedure also serves as a check on the coefficients associated with the different cases considered. In addition, the results for each degree of approximation is given in terms of expressions proportional to $f(b)\, e^{\pm i b}$ and $f'(b)\, e^{\pm 2ib}$, where $f(b)$ is a polynomial in $\underline{b}$ ($\underline{b}$ is a dimensionless parameter defined by $b = \kappa R$). Also, the final results are given in terms of functions of R (R is defined as the distance between the atoms) with an explicit R^{-1} dependence to show the modifications to the electrostatic interaction energy due to the electromagnetic field interactions.

The total interaction energy of the system may now be written as

$$\Delta E = e^4 \left\{ \Delta E_{d-d} + \Delta E_{d-q} + \Delta E_{q-q} \right\} \quad , \tag{236}$$

where each of the above quantities is defined in equations (162), (201), and (235). In addition, these quantities are expressed as sums of terms defined by $X(j)^{(i)}$ which correspond to various types of interactions between the electrostatic and field operators. In general, the breakdown is as follows: The electrostatic interactions are defined by $X(0)^{(i)}$, $i = 1, 2, 3$. The terms resulting solely from electromagnetic field interactions are represented by $X(1)^{(i)}$. These terms contain the interactions due to the second-order electromagnetic field term in the Hamiltonian, which is proportional to $\vec{A}(\vec{\rho}) \cdot \vec{A}(\vec{\rho})$. The next group of terms, denoted by $X(2)^{(i)}$, includes interactions resulting from considering both the first and second order terms in the radiation field perturbation given by $\vec{A}(\vec{\rho}) \cdot \vec{P}(\vec{r})$ and $\vec{A}(\vec{\rho}) \cdot \vec{A}(\vec{\rho})$. If the problem had been treated using only the first-order term $\vec{A}(\vec{\rho}) \cdot \vec{P}(\vec{r})$ in the Hamiltonian, then $X(1)^{(i)}$ and $X(2)^{(i)}$ would not have entered into the discussion. The terms resulting from the interaction between the electrostatic interaction operator $H_q^{(2)}$ and the field operator $\vec{A}(\vec{\rho}) \cdot \vec{P}(\vec{r})$ are denoted by $X(3)^{(i)}$. Finally, the terms resulting solely from the field operator $\vec{A}(\vec{\rho}) \cdot \vec{P}(\vec{r})$ are given by $X(4)^{(i)}$. If the problem had been treated considering only the first-order field operator $\vec{A}(\vec{\rho}) \cdot \vec{P}(\vec{r})$ and the electrostatic interaction operator $H_q^{(2)}$, then only $X(3)^{(i)}$ and $X(4)^{(i)}$ would have contributed to the interaction energy. In this way, the various contributions to the interaction energy may be studied separately.

In subsequent discussions, the dipole-dipole case as well as the higher approximations are again considered. The behavior for large and small R ($R \gtrless \lambda\!\!\!^{-}$) for the dipole-dipole case is considered. The dipole-quadrupole result shown in equation (201) is expressed in terms of polynomials of the form $f(b)\, e^{\pm i b}$, $f'(b)\, e^{\pm 2 i b}$. A further transformation in terms of real quantities $f(y)\, e^{-y}$ and $f'(y)\, e^{-2y}$ is made on the resulting expressions. The results are then examined for the limiting case of large R. The small R case is immediate since the radiation interaction terms contain a coefficient $\underline{a}^3$, which for small R ($a = R/\lambda\!\!\!^{-}$) causes these terms to vanish leaving only the term $X(0)^{(2)}$, which corresponds to the electrostatic interaction only. [See equation (246).] Finally the quadrupole-quadrupole results are considered again and are expressed in terms of polynomials in $\underline{b}$, as for the previous cases.

Dipole-Dipole Approximations

The first check on this calculation is provided by the comparison of the results obtained here with those given by Casimir and Polder, and others. The expression for the dipole-dipole approximation generated here and given by equation (163) is shown to correspond explicitly to the results reported by Power and Zienau [4]. In obtaining this first-order result by means of straightforward stationary state perturbation theory, one also obtains additional information regarding the types of interactions involved in the overall result. For instance, one can show explicitly how the electromagnetic field interactions combine with the electrostatic interaction to absorb the factor resulting from the purely electrostatic interaction, thus allowing one to write the interaction energy ΔE_{d-d} as in equation (163). One also can show precisely how the contributions from the integrals over $f(b)\, e^{\pm i b}$ are eliminated by the residues at $b = 0$ of the integrals over $f'(b)\, e^{\pm 2 i b}$. Also, these residues give a factor which exactly cancels the contribution from $X(0)^{(1)}$. [See equation (163).] The resulting expression for ΔE_{d-d} is then found to result only from the integrals containing $f'(b)\, e^{\pm 2 i b}$. It is for this reason that the higher order results are given in terms of integrals over $e^{\pm i b}$ and $e^{\pm 2 i b}$.

The behavior of ΔE_{d-d} [defined in equation (164)] for small and large R is of interest. The comparison of the magnitude of R discussed here is made with respect to the characteristic wavelength λ corresponding to the frequency associated with the $1s \rightarrow 2p$ atomic transition. Using the relations $(E_1 - E_0) = \hbar 2\pi\nu$, $c = \lambda\nu$, one obtains the connection between λ and R, given by $(E_1 - E_0)R/\hbar c = (2\pi/\lambda)R$. In addition, if one defines $\lambdabar = \lambda/2\pi$, then $a = R/\lambdabar$. Thus, in the case in which the atoms are separated by a distance R such that $R >> \lambdabar$, the result given in equation (164) becomes

$$\Delta E_{d-d}(R >> \lambdabar) = -\frac{4\,(E_1 - E_0)^2 \langle r_1^2\rangle\langle r_2^2\rangle}{(3)^2 \pi R^2 (\hbar c)^3}$$

$$\times \int_0^\infty \frac{u^4\,du\,e^{-2uR}}{\left[(E_1 - E_0)/\hbar c\right]^4}$$

$$\times \left[1 + \frac{2}{(uR)} + \frac{5}{(uR)^2} + \frac{6}{(uR)^3} + \frac{3}{(uR)^4}\right] \quad . \tag{237}$$

The above result is obtained by writing the denominator of the integrand in equation (164) as $\left[\{(E_1 - E_0)\ R/\hbar c\}^2 + \{uR\}^2\right]^2$ and then neglecting $\{uR\}$. This is allowed since $(E_1 - E_0)R/\hbar c >> 1$ and the leading contributions to the integral in question result from small values of $\{uR\}$ due to the exponential factor $e^{-2(uR)}$. This is the same as neglecting $(\hbar c\kappa)$ or $(\hbar c\kappa')$ in favor of $(E_1 - E_0)$ in the denominators of the form $\left[(E_1 - E_0) + \hbar c\kappa\right]$ found in the expression for ΔE_{d-d} given by equation (134). There the major contribution to the integrals over κ and κ' comes from those values of κ and κ' such that κ, $\kappa' << (E_1 - E_0)/\hbar c$ on account of the exponential factors $e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}$ in the integrals [10]. Factoring out R^{-5} from the integrand of equation (237) and rearranging factors, one obtains

$$\Delta E_{d-d}(R >> \lambda\!\!\!^{-}) = -\frac{4\hbar c \langle r_1^2\rangle\langle r_2^2\rangle}{(3)^2 \pi R^7 (E_1 - E_0)^2}$$

$$\times \int_0^\infty (R\,du)\; e^{-2Ru} \left\{ (Ru)^4 + 2(Ru)^3 + 5(Ru)^2 + 6(uR) + 3 \right\} \quad . \tag{238}$$

Integrating term by term, using the integral formula $\int_0^\infty x^n e^{-tx}\,dx = n!/t^{n+1}$, the integral factor in equation (238) is evaluated, and the resulting expression is

$$\Delta E_{d-d}(R >> \lambda\!\!\!^{-}) = -\frac{4\hbar c \langle r_1^2\rangle\langle r_2^2\rangle}{(3)^2 \pi R^7 (E_1 - E_0)^2}\left(\frac{23}{4}\right) \quad . \tag{239}$$

Casimir and Polder [1] give this result in terms of the static polarizabilities of the atoms defined by $\alpha(I) \equiv \frac{2e^2 \langle r_1^2\rangle}{3(E_1 - E_0)}$. Hence, including $\underline{e}^4$ in the final result for ΔE_{d-d} and rearranging numerical factors, equation (239) can be shown to be equal to equation (56) of Casimir and Polder's paper [1]. Equation (239) shows explicitly the R^{-7} behavior of ΔE_{d-d} when the internuclear separation distance R is large in comparison with the characterisitic wavelength $\lambda\!\!\!^{-}$. Equation (239) may be put in a simpler form by expressing it in terms of $X(0)^{(1)}$ as follows:

$$\Delta E_{d-d}(R >> \lambda\!\!\!^{-}) = \frac{23\hbar c\, X(0)^{(1)}}{3\pi R (E_1 - E_0)} \quad . \tag{240}$$

Letting $y = uR$ in equation (163), one obtains

$$\Delta E_{d-d} = X(0)^{(1)} \left\{ \frac{4\,a^3}{3\,\pi} \int_0^{\infty} \frac{R\,du\,\left\{(uR)^4 + 2(uR)^3 + 5(uR)^2 + 6(uR) + 3\right\} e^{-2uR}}{\left[a^2 + (uR)^2\right]^2} \right\},$$

$$= -\frac{\langle r_1^2 \rangle \langle r_2^2 \rangle}{3(E_1 - E_0) R^6} \left\{ \mathcal{G}^{(1)}(a) \right\} \quad . \tag{241}$$

Comparison of equations (240) and (241) shows that for large R, $\mathcal{G}^{(1)}(a)$ decreases monotonically with increasing R (Fig. 15).

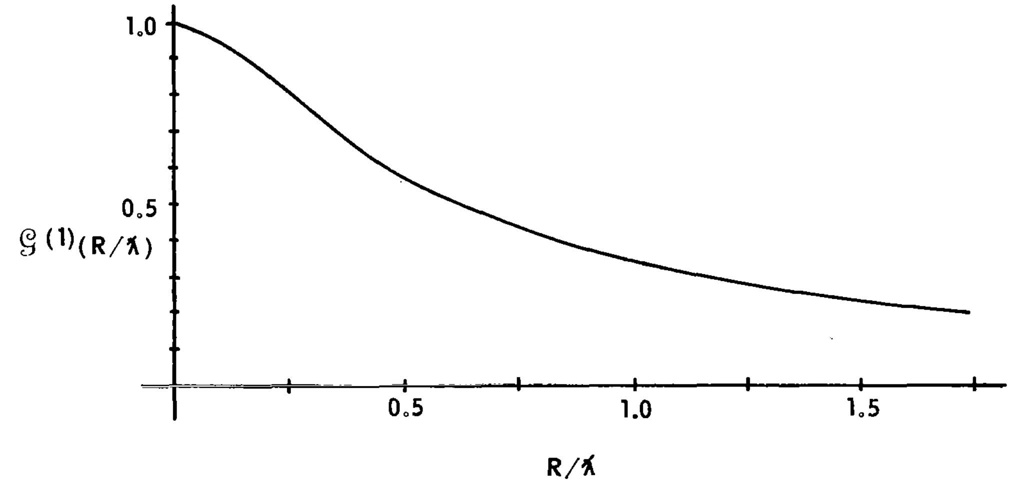

Figure 15. Behavior of the correction factor $\mathcal{G}^{(1)}(R/\chi)$ for various internuclear separation distance R/χ.

The behavior of ΔE_{d-d} for small R may be obtained by considering the factors of equation (164) as follows [10]. The denominator consists of two small quantities; thus, one cannot neglect one against the other. On the other hand when R is small, e^{-2uR} may be replaced by unity since the leading contributions to the integral in equation (164) result for small values of (uR). Finally, the leading term in the polynomial in (uR) corresponds to $(uR)^{-4}$. With these modifications equation (164) becomes

$$\Delta E_{d\text{-}d}(R << \lambda\!\!\!^{-}) = -\frac{4(E_1 - E_0)^2 \langle r_1^2\rangle\langle r_2^2\rangle}{3\pi R^6 (\hbar c)^3} \int_0^{\infty} \frac{du}{\left[\{(E_1 - E_0)/\hbar c\}^2 + u^2\right]^2} \quad . \tag{242}$$

Writing the integral as $\int_0^{\infty} \frac{\{(E_1 - E_0)/\hbar c\}^2 du}{\left[\{(E_1 - E_0)/\hbar c\}^2 + u^2\right]^2}$, and using the integral formula $\int_0^{\infty} a^2 dx/[a^2 + x^2]^2 = \pi/2a^2$, equation (242) reduces to

$$\Delta E_{d\text{-}d}(R << \lambda\!\!\!^{-}) = \left[-\frac{\langle r_1^2\rangle\langle r_2^2\rangle}{3(E_1 - E_0) R^6} \right] \quad .$$

To express the above result in more familiar units, one needs to include the factor $\underline{e}^4$, as indicated in equation (236). Using the following relations, [see equation (86)]:

$$\langle r^{2\ell}\rangle = \frac{(2\ell + 2)!}{2}\left(\frac{a_0}{2Z}\right)^{2\ell} \quad , \quad E_\alpha = -\frac{Z^2 e^2}{2 a_0 \alpha^2} \quad ,$$

and including the $\underline{e}^4$ factor, $\Delta E_{d\text{-}d}(R << \lambda\!\!\!^{-})$ becomes

$$\begin{aligned} \Delta E^{(1)} &= e^4 \Delta E_{d\text{-}d}(R << \lambda\!\!\!^{-}) \\ &= (-8)\left(\frac{e^2}{a_0}\right)\left(\frac{1}{Z}\right)^6\left(\frac{a_0}{R}\right)^6 \quad . \end{aligned} \tag{243}$$

Note that when $(E_1 - E_0)$ is replaced by an average energy [6], the (-8) factor in equation (243) becomes (-6). Equation (243) is just the result obtained when only electrostatic interactions are considered; it corresponds to the London-van der Waal's interaction energy in the absence of radiation fields. Thus, in the limit of small R, $\mathcal{G}^{(1)}(a)$ goes to unity, showing that for small separations the interactions with the radiation field are unimportant and for large separations the introduction of the radiation field gives rise to a weakening of the van der Waal's force.[14]

The behavior of $\mathcal{G}^{(1)}(R/\lambda)$ for various R values $(R >> a_0)$ is illustrated [1] in Figure 15.

Dipole-Quadrupole Approximations

The detailed analysis of the higher approximations is not as straightforward as in the dipole-dipole case. Before one can analyze the equations corresponding to the dipole-quadrupole order interaction energy ΔE_{d-q} given by equation (201), one needs to simplify this expression by substituting the definitions for $\mathcal{F}$, $\mathcal{F}_2$, ... etc. Analysis of equation (201) shows that each $X(j)^{(2)}$ consists of a group of elements having the same functional dependence as in the dipole-dipole approximation, but with the powers of $\underline{b}$ in the various denominators decreased from b^{-4} to b^{-2}. In addition to these terms, each group $X(j)^{(2)}$, $j = 1, 2, 4$, contains a set of "new" quantities defined in terms of F_3, $\mathcal{F}$, $\mathcal{F}_2$.

Using the relations given in equation (201) and the following equalities:

$$\left\{ 12\,\mathcal{F} + 36\,\mathcal{F}_2 - (3)(52)\,F_3 \right\} = 12\,(\mathcal{F} - 4\,F_3) + 36\,(\mathcal{F}_2 - 3\,F_3) \quad ,$$

$$\left\{ 4\,\mathcal{F}\mathcal{F}^- + 6\,\mathcal{F}_2\mathcal{F}_2^- + (2)(26)\,F_3\,F_3^+ \right\} = 4\left\{ \mathcal{F}\mathcal{F}^- + 4\,F_3\,F_3^+ \right\}$$

$$+ 6\left\{ \mathcal{F}_2\mathcal{F}_2^- + 6\,F_3\,F_3^+ \right\} \quad ,$$

$$\left\{ \mathcal{F} - 4\,F_3 \right\} = \left\{ \mathcal{F}_2 - 3\,F_3 \right\} \quad ,$$

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14. This effect was proposed by Verwey, Overbeck and Nes in their book, Theory of the Stability of Lyophobic Colloids (Elsevier, Amsterdam, 1948) and led Casimir and Polder to consider the problem.

the expression for ΔE_{d-q} defined by equation (201) becomes

$$\Delta E_{d-q} = X(0)^{(2)} - \frac{2^2 a^3 X(0)^{(2)}}{(3)^3 5\pi}\left[\int_0^\infty \frac{[6b^4 + 4ab^3 + a^2b^2]}{a(a+b)^2}\left\{F + 2G\right\} db \right.$$

$$+ 12\int_0^\infty \frac{[2b^3 - ab^2]}{b^2(a+b)^2}\left\{\mathcal{F} - 4F_3\right\} db + 2i\int_0^\infty \frac{[4ab^6 + a^2b^5]}{a(a+b)^2}\left\{F F^+ + 2GG^+\right\} db$$

$$\left. - 8i\int_0^\infty \frac{b^5\left\{\mathcal{F}\mathcal{F}^- + 4F_3F_3^+\right\} db}{b^2(a+b)} + 6i\int_0^\infty \frac{ab^5}{b^2(a+b)^2}\left\{\mathcal{F}_2\mathcal{F}_2^- + 6F_3F_3^+\right\} db\right], \quad (244)$$

where the above functions are defined as follows[15]:

$$\left\{F + 2G\right\} = \frac{1}{2ib^3}\left[(b^2 + 3ib - 3)e^{ib} - (b^2 - 3ib - 3)e^{-ib}\right],$$

$$\left\{\mathcal{F} - 4F_3\right\} = \frac{1}{2ib^3}\left[(ib^3 - 6b^2 - 15ib + 15)e^{ib} + (ib^3 + 6b^2 - 15ib - 15)e^{-ib}\right],$$

$$\left\{F F^+ + 2GG^+\right\} = \frac{1}{4i^2b^6}\left[(b^4 + 2ib^3 - 5b^2 - 6ib + 1)e^{2ib} - (b^4 - 2ib^3 - 5b^2 + 6ib + 1)^{-2ib}\right],$$

$$\left\{\mathcal{F}\mathcal{F}^- + 4F_3F_3^+\right\} = \frac{1}{4i^2b^6}\left[(-b^6 - 4ib^5 + 14b^4 + 42ib^3 - 81b^2 - 90ib + 45)e^{2ib}\right.$$
$$\left. - (-b^6 + 4ib^5 + 14b^4 - 42ib^3 - 81b^2 + 90ib + 45)e^{-2ib}\right],$$

$$\left\{\mathcal{F}_2\mathcal{F}_2^- + 6F_3F_3^+\right\} = \frac{1}{4i^2b^6}\left[(-b^6 - 6ib^5 + 27b^4 + 84ib^3 - 162b^2 - 180ib + 90)e^{2ib}\right.$$
$$\left. - (-b^6 + 6ib^5 + 27b^4 - 84ib^3 - 162b^2 + 180ib + 90)e^{-2ib}\right].$$

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15. These relations are obtained by using the various definitions for F, G, ... $\mathcal{F}_2$, and forming the appropriate sums and products.

Comparison of equation (244) to the dipole-dipole results given by equation (162) shows explicitly the terms of equation (244) having the same $f(b)\, e^{\pm i b}$, $f'(b)\, e^{\pm 2 i b}$ dependence as in the dipole-dipole case.

Using the techniques outlined in Appendix C, the b-integrals appearing in equation (244) are individually evaluated. Incorporating the results of these transformations equation (244) becomes[16]

$$\Delta E_{d-q} = X(0)^{(2)} \left[1 - \frac{2^2 a^3}{(3)^3 (5\pi)} \left\{ -2\left(\frac{3\pi}{4a}\right) - 2 \int_0^\infty \frac{(4y^2 - 2a^2)}{(a^2+y^2)^2} (y^2 + 3y + 3)\, e^{-y}\, dy \right.\right.$$

$$- \left(\frac{9\pi}{a}\right) + 24 \int_0^\infty \frac{(y^2 - 2a^2)}{y^2 (a^2+y^2)^2} (y^3 + 6y^2 + 15y + 15)\, e^{-y}\, dy$$

$$+ 2\left(\frac{3\pi}{4a}\right) - \int_0^\infty \frac{(4y^2 - 2a^2)}{(a^2+y^2)^2} (y^4 + 2y^3 + 5y^2 + 6y + 3)\, e^{-2y}\, dy$$

$$- 2\left(\frac{9\pi}{a}\right) - 4 \int_0^\infty \frac{dy}{y^2 (a^2+y^2)} (y^6 + 4y^5 + 14y^4 + 42y^3 + 81y^2 + 90y + 45)\, e^{-2y}$$

$$\left.\left. + 3\left(\frac{9\pi}{a}\right) + 6 \int_0^\infty \frac{a^2\, dy}{y^2 (a^2+y^2)^2} (y^6 + 6y^5 + 27y^4 + 84y^3 + 162y^2 + 180y + 90)\, e^{-2y} \right\} \right]. \tag{245}$$

The constant factors in the above equation are the residues at the origin $(b = 0)$ of the various terms considered. Adding these constants, one sees that their sum is zero. In addition, they combine in pairs; the residues of the first and third integrals proportional to $(y^2 \ldots)\, e^{-y}$ and $(y^4 \ldots)\, e^{-2y}$ add up to zero, and the "new" terms proportional to $(y^3 \ldots)\, e^{-y}$ and $(y^6 \ldots)\, e^{-2y}$ also add to zero. Considering these terms in two groups, one sees that the group associated with the "new" terms has an additional y^{-2} factor, which gives rise

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16. The ordering of terms in equations (244) and (245) is the same to show explicitly the results of the various integrations and transformations.

to a lower R^{-1} dependence. Rearranging[17] terms in equation (245) to reflect the preceding groupings and excluding the constants, ΔE_{d-q} may be written as follows:

$$\Delta E_{d-q} = X(0)^{(2)} + \frac{2^2 a^3 X(0)^{(2)}}{(3)^3(5\pi)} \left\{ 2 \int_0^\infty \frac{(4y^2 + 3a^2)}{(a^2+y^2)^2} (y^2 + 3y + 3)\, e^{-y}\, dy \right.$$

$$\left. + \int_0^\infty \frac{(4y^2 - 2a^2)}{(a^2+y^2)^2} (y^4 + 2y^3 + 5y^2 + 6y + 3)\, e^{-2y} \right\}$$

$$\frac{a^3 X(0)^{(2)}}{(3)^3(5\pi)} \left\{ -24 \int_0^\infty \frac{(y^2 - 2a^2)}{y^2(a^2+y^2)^2} (y^3 + 6y^2 + 15y + 15)\, e^{-y} \right.$$

$$- 2 \int_0^\infty \frac{a^2\, dy}{y^2(a^2+y^2)^2} (y^6 + 10y^5 + 53y^4 + 168y^3 + 324y^2 + 360y + 180)\, e^{-2y}$$

$$\left. + 4 \int_0^\infty \frac{y^2\, dy}{y^2(a^2+y^2)^2} (y^6 + 4y^5 + 14y^4 + 42y^3 + 81y^2 + 90y + 45)\, e^{-2y} \right\}$$

$$= X(0)^{(2)} + X_1^{(2)}(a) + X_2^{(2)}(a) \tag{246}$$

where the new functions $X_1^{(2)}(a)$ and $X_2^{(2)}(a)$ are defined in the expression for ΔE_{d-q}. Subsequent calculations will show the significance of the above definitions. Comparison of equation (246) to its dipole-dipole counterpart given by equation (164) shows that, unlike the dipole-dipole case, equation (246) consists of three separate terms, with one of them being solely due to the electrostatic interaction between atoms and the others arising from the interactions between the electrostatic and electromagnetic fields.

In order to further analyze the results for the dipole-quadrupole case, one needs to examine the large R ($R >> \lambda$) behavior of equation (246). Following the same procedure as that used for equations (237) through (243) and

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17. The last two terms in equation (245) are combined by first getting $y^2(a^2 + y^2)^2$ as the common denominator.

collecting all the terms having the same y^n power and similar exponential factor, the preceding expression becomes

$$\Delta E_{d-q}(R >> \lambda)$$

$$= X(0)^{(2)} \left[1 + \frac{2^2 a^3}{(3)^3 (5\pi)} \left\{ -\frac{6}{a_2} \int_0^\infty (y^2 + 11y + 51 + 120y^{-1} + 120y^{-2})\, e^{-y}\, dy \right.\right.$$

$$- \frac{2}{a^2} \int_0^\infty (2y^4 + 12y^3 + 58y^2 + 174y + 327 + 360y^{-1} + 180y^{-2})\, e^{-2y}\, dy$$

$$\left.\left. + \frac{4}{a^4} \int_0^\infty (y^6 + 10y^5 + 14y^4 + 42y^3 + 81y^2 + 90y + 45)\, e^{-2y}\, dy \right\} \right] . \tag{247}$$

Evaluation of the above integrals is accomplished in the following way: For the integrals having positive powers in y, one simply uses the formula $\int_0^\infty x^n e^{-tx}\, dx = (n!/t^{n+1})$. The integrals containing negative powers of y may be combined by letting $y \to 2y$ in the integral containing e^{-y}, resulting in the relations

$$\int_0^\infty y^{-1} e^{-y}\, dy = \int_0^\infty y^{-1} e^{-2y}\, dy \quad ,$$

$$\int_0^\infty y^{-2} e^{-y}\, dy = \frac{1}{2} \int_0^\infty y^{-2} e^{-2y}\, dy \quad .$$

Doing this, one finds that the sum of these integrals is identically zero. Performing the indicated operations and combining the resulting factors into two groups having $\underline{a}$ and $(1/a)$ coefficients, equation (247) becomes

$$\Delta E_{d-q}(R >> \chi) = X(0)^{(2)} \left[1 + \frac{2^2 a^3}{(3)^3(5\pi)} \left\{ \left(-\frac{71}{a^2}\right) + \left(\frac{927}{a^4}\right) \right\} \right]$$

$$= \left\{ X(0)^{(2)} - \frac{284\, a}{135\pi} X(0)^{(2)} + \frac{1854}{135\pi} \frac{X(0)^{(2)}}{a} \right\} \quad . \tag{248}$$

Using the definitions for $\underline{a}$ and $X(0)^{(2)}$, one can see that $a\,X(0)^{(2)} \sim 1/R^7$ and $X(0)^{(2)}/a \sim 1/R^9$; hence, the above expression may be put into the following form

$$\Delta E_{d-q}(R >> \chi) = \frac{A}{R^7} + \frac{B}{R^8} + \frac{C}{R^9} \quad , \tag{249}$$

where

$$A = \frac{284}{135\pi\hbar c} \langle r_1^2\rangle\langle r_2^4\rangle \quad ,$$

$$B = -\frac{\langle r_1^2\rangle\langle r_2^4\rangle}{(E_1 - E_0)} \quad ,$$

$$C = -\frac{1854\,\hbar c\ \langle r_1^2\rangle\langle r_2^4\rangle}{135\pi\ (E_1 - E_0)^2} \quad .$$

Equation (249) shows explicitly how the electrostatic interaction term B/R^8 is reinforced by a factor proportional to $1/R^9$ and decreased by a factor proportional to $1/R^7$. To determine the relative magnitude of these factors, one can rewrite the above coefficients in terms of atomic units.

Referring to the equation for ΔE_{d-q} given in terms of factors proportional to R^{-7}, R^{-8}, and R^{-9}, it is of interest to note that this result should be expected from the general form of ΔE_{d-q}, [see equation (246)]. Hence, one may write the interaction energy as follows:

$$\Delta E_{d-q} = \left\{ \frac{\mathcal{F}^{(2)}(R/\lambda)}{R^7} + \frac{\mathcal{X}(0)^{(2)}}{R^8} + \frac{\mathcal{G}^{(2)}(R/\lambda)}{R^9} \right\} , \qquad (250)$$

where the above functions are obtained by simply factoring out a^{-2}, R^{-8}, and a^{-4} from $X_1^{(2)}(a)$, $X(0)^{(2)}$ and $X_2^{(2)}(a)$, respectively. [See equation (246).]

The behavior of the above quantities in equation (250) may be inferred from Figure 15 and by comparison of $\mathcal{F}^{(2)}(R/\lambda)$ and $\mathcal{G}^{(2)}(R/\lambda)$ to the function $\mathcal{G}^{(1)}(R/\lambda)$ of equation (241). Since the functions appearing in ΔE_{d-q} are much more complex than $\mathcal{G}^{(1)}(R/\lambda)$, a computer program would be required to numerically evaluate the integrals to construct the plots corresponding to Figure 15.

Quadrupole-Quadrupole Approximations

The increased complexity of the expression for the quadrupole-quadrupole order interaction energy ΔE_{q-q} given by equation (235) makes it necessary to give only the general expression equivalent to equations (162) and (244) for the dipole-dipole and dipole-quadrupole cases, respectively.

Starting with the expression for ΔE_{q-q} given by equation (235) and recombining the various terms as in the dipole-quadrupole case, ΔE_{q-q} may be written as

$$
\begin{aligned}
\Delta E_{q-q} = X(0)^{(3)} + \frac{a^3\, X(0)^{(3)}}{(3)\,(5)^3\,(7\pi)} \Bigg\{ & \int_0^\infty b^3\, F_3\, db \left[\frac{(21\,b^3 + 20\,a\,b^2 + a^2\,b + a^3)}{3\,a\,(a+b)^2}\right] \\
& + \int_0^\infty b\,(\mathcal{F} - 4\,F_3)\,db \left[\frac{8\,(6\,b^3 + 10\,a\,b^2 - 7\,a^2\,b + 4\,a^3)}{a\,(a+b)^2}\right] \\
& - \int_0^\infty \frac{(f + 6\,\mathcal{F}_4 - 3\,F_3)}{b}\,db \\
& \times \left[\frac{8\,(33\,b^3 + 40\,a\,b^2 - 40\,a^2\,b + 64\,a^3)}{a\,(a+b)^2}\right] \\
& + \int_0^\infty (19\,b^2\,F_2 - 2\,\mathcal{F}_2 + 6\,F_3)\,db \left[\frac{b^2}{a\,(a+b)^2}\right] \\
& + i \int_0^\infty b^6\,db \left[F\,F^{+} + 2\,G\,G^{+}\right] \left[\frac{2\,(40\,b^2 - 19\,a\,b - 38\,a^2)}{3\,(a+b)^2}\right] \\
& + i \int_0^\infty b^6\,db \left[F_2\,F_2^{+} + 2\,G\,G^{+}\right] \left[\frac{40\,b^2 + 47\,a\,b - 50\,a^2}{3\,(a+b)^2}\right] \\
& + i \int_0^\infty b^6\,db \left[(F - G)\,(F^{+} - G^{+})\right] \left[\frac{13\,a^2\,(2\,a + b)}{a\,(a+b)^2}\right] \\
& + i \int_0^\infty b^4\,db \left[\mathcal{F}\mathcal{F}^{-} + 4\,F_3\,F_3^{+}\right] \left[-\frac{80}{3}\right] \\
& + i \int_0^\infty b^4\,db \left[\mathcal{F}_2\,\mathcal{F}_2^{-} + 6\,F_3\,F_3^{+}\right] \left[\frac{8\,(2\,a^2 - 9\,a\,b)}{(a+b)^2}\right] \\
& + i \int_0^\infty b^4\,db \left[G\,G^{+}\right] \left[\frac{32\,a\,b^4}{(a+b)}\right] \\
& + i \int_0^\infty b^2\,db \left[f\,f^{-} + 12\,\mathcal{F}_4\,\mathcal{F}_4^{-} + 24\,F_3\,F_3^{+}\right] \\
& \times \left[\frac{8\,(5\,b^2 - 5\,a\,b + 8\,a^2)}{3\,(a+b)^2}\right] \Bigg\} \; .
\end{aligned}
\tag{251}
$$

The preceding expression is no simpler than equation (235), but it is more useful since the various functions have been regrouped into sets previously considered, which simplifies further analysis. The "new" groupings generated may be expressed in terms of polynomials in $\underline{b}$ using previous techniques. The new combinations required are as follows:

$$\left\{ f + 6\,\mathcal{F}_4 - 3\,F_3 \right\} = \frac{1}{2\,i\,b^3} \left\{ [b^4 + 4\,i\,b^3 - 39\,b^2 - 105\,i\,b - 105]\; e^{i\,b} \right.$$

$$\left. - [b^4 - 4\,i\,b^3 - 39\,b^2 + 105\,i\,b - 105]\; e^{-i\,b} \right\} ,$$

$$\left\{ f\,f^+ + 12\,\mathcal{F}_4\,\mathcal{F}_4^{-1} + 24\,F_3\,F_3^+ \right\}$$

$$= \frac{1}{4\,i^2\,b^6} \left\{ \Big[[b^8 + 8\,i\,b^7 - 40\,b^6 - 144\,i\,b^5 + 384\,b^4 + 768\,i\,b^3 - 1152\,b^2 - 1152\,i\,b + 576] \right.$$

$$+ 12\,[-b^6 - 10\,i\,b^5 + 49\,b^4 + 144\,i\,b^3 - 264\,b^2 - 288\,i\,b + 144]$$

$$+ 24\,[b^4 + 6\,i\,b^3 - 15\,b^2 - 18\,i\,b + 9] \Big]\; e^{2\,i\,b}$$

$$- \Big[[b^8 - 8\,i\,b^7 - 40\,b^6 + 144\,i\,b^5 + 384\,b^4 - 768\,i\,b^3 - 1152\,b^2 + 1152\,i\,b + 576]$$

$$+ 12\,[-b^6 + 10\,i\,b^5 + 49\,b^4 - 144\,i\,b^3 - 264\,b^2 + 288\,i\,b + 144]$$

$$\left. + 24\,[b^4 - 6\,i\,b^3 - 15\,b^2 + 18\,i\,b + 9] \Big]\; e^{-2\,i\,b} \right\} .$$

Using the above relations and the dipole-quadrupole approximation, equation (251) may be further analyzed. It is not necessary to rewrite equation (251) explicitly in terms of polynomials in $\underline{b}$, since only a comparison of this result to previous answers is given. Reference to equations (244) and (251) shows that the quadrupole-quadrupole result contains groups of terms appearing in the previous dipole-quadrupole case but with different polynomials in $\underline{a}$ and $\underline{b}$. Comparison to equation (162) also shows that the quadrupole-quadrupole case again contains terms having the same functional dependence $f(b)\,e^{\pm i\,b}$ as in the dipole-dipole case. Thus, one can see that the results are systematic, in that the higher approximations can always be expressed in terms of previous quantities appropriately modified, plus some "new" terms. An analysis can be made of the dimensionality of the various integral terms of equation (251) in terms of the constant $\underline{a}$. Since $\underline{a}$ is proportional to R, one can see that terms proportional to R^{-7}, R^{-8}, ... R^{-11} are included in the various elements of equation (251). For example, the eighth integral of that equation is an example of terms having an R^{-7} dependence since its value is independent of $\underline{a}$ and its coefficient is $a^3 X(0)^{(3)}$. The rest of the integrals have various factors proportional to $1/a$, $1/a^2$, $1/a^3$ and $1/a^4$, which when multiplied by $a^3 X(0)^{(3)}$ gives rise to the R^{-1} dependence indicated above. Hence, one can always express the results of equation (251) as follows:

$$\Delta E_{q-q} = \left\{ \frac{\mathcal{F}^{(3)}(R/\lambda)}{R^7} + \frac{\mathcal{I}^{(3)}(R/\lambda)}{R^8} + \frac{\mathcal{H}^{(3)}(R/\lambda)}{R^9} + \frac{\mathcal{Q}^{(3)}(R/\lambda)}{R^{10}} + \frac{\mathcal{G}^{(3)}(R/\lambda)}{R^{11}} \right\} \quad . \tag{252}$$

The algebraic form of each of the above functions can be obtained by separating the terms in equation (251), as was done for the dipole-quadrupole approximation. When this is done, one finds that each function is the same as in previous cases with only more complex factors $f(b)\, e^{\pm i b}$. Therefore, their behavior for all R is expected to be like that on Figure 15, with only a more rapid decrease for those terms whose limiting form for large R decreases as R^{-9} and R^{-11}.

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Marshall Space Flight Center, Alabama 35812, April 10, 1970
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APPENDIX A

POLARIZATION VECTOR SUMS

In the course of this calculation, various products involving the polarization vectors $\hat{\epsilon}_\lambda(\vec{\kappa})$ need to be evaluated. To calculate these relations, one defines a coordinate system (Fig. A-1).

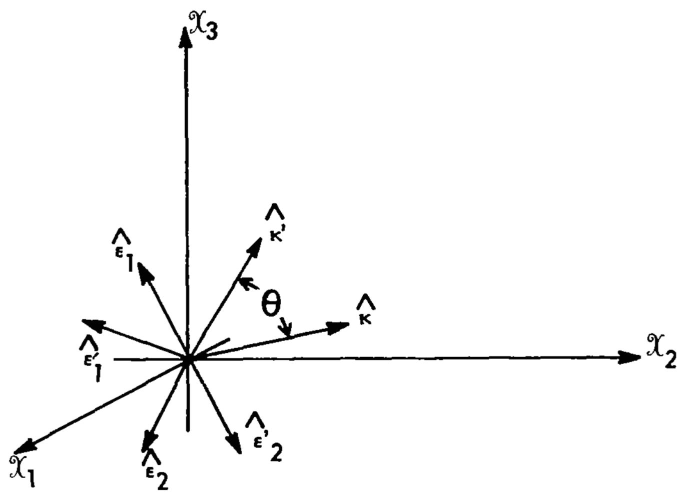

Figure A-1. Polarization vector coordinates.

Using the coordinate system in Figure A-1 and the following unit vector relations:

$$\hat{\epsilon}_1 = \ell_{11}\hat{\mathcal{X}}_1 + \ell_{12}\hat{\mathcal{X}}_2 + \ell_{13}\hat{\mathcal{X}}_3 \quad ,$$

$$\hat{\epsilon}_2 = \ell_{21}\hat{\mathcal{X}}_1 + \ell_{22}\hat{\mathcal{X}}_2 + \ell_{23}\hat{\mathcal{X}}_3 \quad ,$$

$$\hat{\kappa} = \ell_{31}\hat{\mathcal{X}}_1 + \ell_{32}\hat{\mathcal{X}}_2 + \ell_{33}\hat{\mathcal{X}}_3 \quad ,$$

$$\hat{\epsilon}_1 \cdot \hat{\epsilon}_2 = 0, \quad \hat{\epsilon}_1 \cdot \hat{\kappa} = 0, \quad \hat{\epsilon}_2 \cdot \hat{\kappa} = 0,$$

$$\hat{\epsilon}_1 \cdot \hat{\epsilon}_1 = \hat{\epsilon}_2 \cdot \hat{\epsilon}_2 = \hat{\kappa} \cdot \hat{\kappa} = 1 \quad , \tag{A-1}$$

one obtains the various sums needed.

The first sum to be considered is evaluated as follows:

$$\sum_{\lambda=1}^{2} \hat{\epsilon}_{\lambda}(\vec{\kappa}) \cdot \hat{\epsilon}_{\lambda}(\vec{\kappa}) = \hat{\epsilon}_1 \cdot \hat{\epsilon}_1 + \hat{\epsilon}_2 \cdot \hat{\epsilon}_2 = 2 \quad . \tag{A-2}$$

The next sum is given by

$$\sum_{\lambda=1}^{2} \sum_{\lambda'=1}^{2} \left\{ \hat{\epsilon}_{\lambda}(\vec{\kappa}) \cdot \hat{\epsilon}_{\lambda'}(\vec{\kappa}') \right\} \left\{ \hat{\epsilon}_{\lambda}(\vec{\kappa}) \cdot \hat{\epsilon}_{\lambda'}(\vec{\kappa}') \right\}$$

$$= \left\{ \hat{\epsilon}_1(\hat{\kappa}) \cdot \hat{\epsilon}_1(\hat{\kappa}') \right\}^2 + \left\{ \hat{\epsilon}_1(\hat{\kappa}) \cdot \hat{\epsilon}_2(\hat{\kappa}') \right\}^2$$

$$+ \left\{ \hat{\epsilon}_2(\hat{\kappa}) \cdot \hat{\epsilon}_1(\hat{\kappa}') \right\}^2 + \left\{ \hat{\epsilon}_2(\hat{\kappa}) \cdot \hat{\epsilon}_2(\hat{\kappa}') \right\}^2 \quad .$$

In terms of the unit vectors of equation (A-1), the above becomes

$$\sum_{ij} \left\{ \ell_{1i} \ell'_{1i} \ell_{1j} \ell'_{1j} + \ell_{1i} \ell'_{2i} \ell_{1j} \ell'_{2j} \right.$$

$$\left. + \ell_{2i} \ell'_{1i} \ell_{2j} \ell'_{1i} + \ell_{2i} \ell'_{2i} \ell_{2j} \ell'_{2j} \right\} \quad .$$

Adding and subtracting $\sum_{ij} \ell_{1i} \ell_{1j} \ell'_{3i} \ell'_{3j}$ and rearranging factors, this expression becomes

$$\left\{ \sum_{ij\kappa} \ell_{1i} \ell_{1j} \ell'_{\kappa i} \ell'_{\kappa j} - \sum_{ij} \ell_{1i} \ell_{1j} \ell'_{3i} \ell'_{3j} \right.$$

$$\left. + \sum_{ij\kappa} \ell_{2i} \ell_{2j} \ell'_{\kappa i} \ell'_{\kappa j} - \sum_{ij} \ell_{2i} \ell_{2j} \ell'_{3i} \ell'_{3j} \right\} \quad .$$

Combining the sums over i, j and using the sum rule for orthonormal systems $\sum_{\kappa} \ell_{\kappa i} \ell_{\kappa j} = \delta_{ij}$, the above quantities combine into

$$\sum_{ij} \ell_{1i} \ell_{1j} \left\{ \delta_{ij} - \ell'_{3i} \ell'_{3j} \right\} + \sum_{ij} \ell_{2i} \ell_{2j} \left\{ \delta_{ij} - \ell'_{3i} \ell'_{3j} \right\} .$$

Adding and subtracting $\sum_{ij} \ell_{3i} \ell_{3j} \left\{ \delta_{ij} - \ell'_{3i} \ell'_{3j} \right\}$, one obtains

$$\sum_{ij\kappa} \ell_{\kappa i} \ell_{\kappa j} \left\{ \delta_{ij} - \ell'_{3i} \ell'_{3j} \right\} - \sum_{ij} \ell_{3i} \ell_{3j} \left\{ \delta_{ij} - \ell'_{3i} \ell'_{3j} \right\} ,$$

Summing over κ in the first sum, one obtains

$$\sum_{ij} \delta_{ij} \left\{ \delta_{ij} - \ell'_{3i} \ell'_{3j} \right\} ,$$

which when combined with the second term, gives

$$\sum_{\lambda=1}^{2} \sum_{\lambda'=1}^{2} \left\{ \hat{\epsilon}_{\lambda}(\hat{\kappa}) \cdot \hat{\epsilon}_{\lambda'}(\hat{\kappa}') \right\} \left\{ \hat{\epsilon}_{\lambda}(\hat{\kappa}) \cdot \hat{\epsilon}_{\lambda'}(\hat{\kappa}') \right\}$$

$$= \sum_{ij} \left\{ \delta_{ij} - (\hat{\kappa})_i (\hat{\kappa})_j \right\} \left\{ \delta_{ij} - (\hat{\kappa}')_i (\hat{\kappa}')_j \right\} , \tag{A-3}$$

where one uses the relation $\hat{\kappa} = (\hat{\kappa})_1 \hat{\mathfrak{X}}_1 + (\hat{\kappa})_2 \hat{\mathfrak{X}}_2 + (\hat{\kappa})_3 \hat{\mathfrak{X}}_3$ and the one in equation (A-1). Equation (A-3) may be expressed in terms of the angle between $\hat{\kappa}$ and $\hat{\kappa}'$ defined as Θ. To find this relationship, one takes the result in equation (A-3) and expands it over i and j. Hence,

$$\sum_{ij} \left(\delta_{ij} - \ell_{3i}\ell_{3j}\right)\left(\delta_{ij} - \ell'_{3i}\ell'_{3j}\right)$$

$$= 3 - \left(\ell_{31}\ell_{31} + \ell_{32}\ell_{32} + \ell_{33}\ell_{33}\right) - \left(\ell'_{31}\ell'_{31} + \ell'_{32}\ell'_{32} + \ell'_{33}\ell'_{33}\right)$$

$$+ \left(\ell_{31}\ell_{31}\ell'_{31}\ell'_{31} + \ell_{32}\ell_{32}\ell'_{32}\ell'_{32} + \ell_{33}\ell_{33}\ell'_{33}\ell'_{33}\right)$$

$$+ 2\left(\ell_{31}\ell_{32}\ell'_{31}\ell'_{32} + \ell_{31}\ell_{33}\ell'_{31}\ell'_{33} + \ell_{32}\ell_{33}\ell'_{32}\ell'_{33}\right) \quad .$$

Combining the above terms, one obtains

$$\Big\{ 1 + \sum_{i}\left(\ell_{3i}\ell'_{3i}\right)^2 + 2\left(\ell_{31}\ell'_{31}\right)\left(\ell_{32}\ell'_{32}\right) + 2\left(\ell_{31}\ell'_{31}\right)\left(\ell_{33}\ell'_{33}\right)$$

$$+ 2\left(\ell_{32}\ell'_{32}\right)\left(\ell_{33}\ell'_{33}\right) \Big\} \quad .$$

Analysis of the last three terms in the above expression shows that these elements correspond to the cross terms of the product $\sum_{ij}\left(\ell_{3i}\ell'_{3i}\right)\left(\ell_{3j}\ell'_{3j}\right)$, and that the term $\sum_{i}\left(\ell_{3i}\ell'_{3i}\right)^2$ corresponds to the sum of the squares of this product. Hence,

$$\sum_{\lambda=1}\sum_{\lambda'=1}\left\{\hat{\epsilon}_{\lambda}(\hat{\kappa})\cdot\hat{\epsilon}_{\lambda'}(\hat{\kappa}')\right\}\left\{\hat{\epsilon}_{\lambda}(\hat{\kappa})\cdot\hat{\epsilon}_{\lambda'}(\hat{\kappa}')\right\} \quad ,$$

$$= \left\{1 + \sum_{ij}\left(\ell_{3i}\ell'_{3i}\right)\left(\ell_{3j}\ell'_{3j}\right)\right\} = \left\{1 + \cos^2\Theta\right\} \quad . \qquad \text{(A-4)}$$

The next sum consists of polarization vector components given by [10]

$$\sum_{\lambda=1}^{2}\left[\hat{\epsilon}_{\lambda}(\hat{\kappa})\right]_i\left[\hat{\epsilon}_{\lambda}(\hat{\kappa})\right]_j = \left(\hat{\epsilon}_1\right)_i\left(\hat{\epsilon}_1\right)_j + \left(\hat{\epsilon}_2\right)_i\left(\hat{\epsilon}_2\right)_j$$

$$= \sum_{\kappa} \ell_{\kappa i}\,\ell_{\kappa j} - \ell_{3i}\,\ell_{3j}$$

$$= \left\{\delta_{ij} - (\hat{\kappa})_i(\hat{\kappa})_j\right\} \quad . \tag{A-5}$$

The next term to be evaluated consists of products of the form considered above and given by

$$\sum_{\lambda=1}\sum_{\lambda'=1}\left\{\left[\hat{\epsilon}_{\lambda}(\vec{\kappa})\right]_i\left[\hat{\epsilon}_{\lambda'}(\hat{\kappa}')\right]_j\left[\hat{\epsilon}_{\lambda}(\vec{\kappa})\right]_k\left[\hat{\epsilon}_{\lambda'}(\hat{\kappa}')\right]_\ell\right\}$$

$$= \left\{\delta_{ik} - (\hat{\kappa})_i(\hat{\kappa})_k\right\}\left\{\delta_{ij} - (\hat{\kappa}')_j(\hat{\kappa}')_\ell\right\} \quad . \tag{A-6}$$

The last sum to be evaluated consists of combinations of terms previously considered. It is evaluated by taking

$$\sum_{\lambda=1}^{2}\sum_{\lambda'=1}^{2}\left\{\hat{\epsilon}_{\lambda}(\hat{\kappa})\cdot\hat{\epsilon}_{\lambda'}(\hat{\kappa}')\right\}\left[\hat{\epsilon}_{\lambda}(\hat{\kappa})\right]_i\left[\hat{\epsilon}_{\lambda'}(\hat{\kappa}')\right]_j$$

$$= \sum_{\kappa}\Big(\ell_{1k}\,\ell'_{1k}\,\ell_{1i}\,\ell'_{1j} + \ell_{1k}\,\ell'_{2k}\,\ell_{1i}\,\ell'_{2j}$$

$$+ \ell_{2k}\,\ell'_{1k}\,\ell_{2i}\,\ell'_{1j} + \ell_{2k}\,\ell'_{2k}\,\ell_{2i}\,\ell'_{2j}\Big)$$

$$= \left\{\delta_{ij} - (\hat{\kappa}')_i(\hat{\kappa}')_j - (\hat{\kappa})_i(\hat{\kappa})_j + (\hat{\kappa})_i(\hat{\kappa}')_j(\hat{\kappa}\cdot\hat{\kappa}')\right\} \quad . \tag{A-7}$$

APPENDIX B

PROPAGATION AND POLARIZATION VECTOR ANGULAR INTEGRALS

Introduction

In this appendix, the integrals over the angular coordinates of $\vec{\kappa}$ and $\vec{\kappa}'$ are evaluated in terms of functions depending on the magnitude of $\vec{\kappa}$ and $\vec{\kappa}'$. In the course of evaluating these integrals, one uses the following relations:

$$b = \kappa R \quad ,$$

$$\beta = \kappa' R \quad ,$$

$$\hat{\kappa} = \sin\theta \cos\phi \, \hat{e}_1 + \sin\theta \sin\phi \, \hat{e}_2 + \cos\theta \, \hat{e}_3 \quad ,$$

$$x = \pm i \kappa R \cos\theta = \pm i b \cos\theta \quad ,$$

$$\cos\Theta = \cos\theta \cos\theta' + \sin\theta \sin\theta' \cos(\phi - \phi') \quad ,$$

$$\int x^m e^{ax} dx = \frac{x^m e^{ax}}{a} - \frac{m}{a} \int x^{m-1} e^{ax} dx \quad . \qquad \text{(B-1)}$$

The single integral functions over $d\Omega_\kappa$ are evaluated first; then using these results, the double integrals over $d\Omega_\kappa$ and $d\Omega_{\kappa'}$ are considered. Finally, the last section contains the relations satisfied by various terms having exponential factors $\pm i(\vec{\kappa}+\vec{\kappa}') \cdot \vec{R}$ and $\pm i(\vec{\kappa}-\vec{\kappa}') \cdot \vec{R}$.

Evaluation of $\int e^{\pm i\vec{\kappa}\cdot\vec{R}} \cos^n \theta \, d\Omega_\kappa$

The simplest integral to be evaluated corresponds to $\int e^{\pm i\vec{\kappa}\cdot\vec{R}} \, d\Omega_\kappa$. After substituting for the quantities defined in equation (B-1), this integral becomes

$$\int e^{\pm i\vec{\kappa}\cdot\vec{R}} \, d\Omega_\kappa = \int_0^\pi \int_0^{2\pi} e^{\pm x} \sin\theta \, d\theta \, d\phi$$

$$= \left(\frac{2\pi}{\mp i b}\right) \int_{\pm i b}^{\mp i b} e^{\pm x} \, dx = 4\pi \left(\frac{\sin b}{b}\right) \quad . \qquad \text{(B-2)}$$

The next integral to be evaluated is given by $\int e^{\pm i\vec{\kappa}\cdot\vec{R}} \cos\theta \, d\Omega_\kappa$. Using previous definitions, this integral becomes

$$\int e^{-i\vec{\kappa}\cdot\vec{R}} \cos\theta \, d\Omega_\kappa = \frac{2\pi}{-(i b)^2} \int_{-i b}^{+i b} x e^x \, dx$$

$$= 4\pi i \left(\frac{\cos b}{b} - \frac{\sin b}{b^2}\right) \equiv 4\pi i b \, G(b) \quad .$$

Similar operations are used to obtain the corresponding integral with a (+) sign; the results are

$$\int e^{\pm i\vec{\kappa}\cdot\vec{R}} \cos\theta \, d\Omega_\kappa = \mp 4\pi i b \, G(b) \quad . \qquad \text{(B-3)}$$

The next integral is given by $\int e^{\pm i\vec{\kappa}\cdot\vec{R}} \cos^2\theta \, d\Omega_\kappa$. Using the same substitutions as before, this integral gives

$$\int e^{\pm i \vec{\kappa} \cdot \vec{R}} \cos^2 \theta \, d\Omega_\kappa = \frac{2\pi}{(\pm i b)^2} \int_{\pm i b}^{\mp i b} x^2 e^{\pm x} \frac{dx}{(\mp i b)} \quad .$$

Choosing the upper sign in the above expression, one obtains

$$\int e^{+i \vec{\kappa} \cdot \vec{R}} \cos^2 \theta \, d\Omega_\kappa = 4\pi \left\{ \frac{\sin b}{b} + \frac{2 \cos b}{b^2} - \frac{2 \sin b}{b^3} \right\} \quad .$$

Similarly the other integral gives

$$\int e^{-i \vec{\kappa} \cdot \vec{R}} \cos^2 \theta \, d\Omega_\kappa = \int e^{+i \vec{\kappa} \cdot \vec{R}} \cos^2 \theta \, d\Omega_\kappa \quad .$$

Combining these results, one obtains

$$\int e^{\pm i \vec{\kappa} \cdot \vec{R}} \cos^2 \theta \, d\Omega_\kappa = 4\pi \left\{ F(b) + G(b) \right\} \equiv 4\pi \ F_2(b) \quad , \qquad \text{(B-4)}$$

where $F(b) \equiv \frac{\sin b}{b} + G(b)$, and $G(b) \equiv \frac{\cos b}{b^2} - \frac{\sin b}{b^3}$. Further combination yields

$$\int e^{\pm i \vec{\kappa} \cdot \vec{R}} (1 - 3 \cos^2 \theta) = - (2^3 \pi) \left\{ F(b) + 2\, G(b) \right\} \equiv - (2^3 \pi) \ F_3(b) \quad .$$

The next integral to be considered is given by $\int e^{\pm i \vec{\kappa} \cdot \vec{R}} \cos^3 \theta \, d\Omega_\kappa$. Using the same techniques, one obtains

$$\int e^{\pm i\vec{\kappa}\cdot\vec{R}} \cos^3\theta \, d\Omega_\kappa = \mp 4\pi i \left\{ b\,G(b) - \frac{2}{b} F_3(b) \right\} \equiv \mp 4\pi i \, b^{-1} \mathcal{F}_2(b) \quad . \tag{B-5}$$

The next integral is given by $\int e^{\pm i\vec{\kappa}\cdot\vec{R}} \cos^4\theta \, d\Omega_\kappa$. One can show that this integral is equal to

$$\int e^{\pm i\vec{\kappa}\cdot\vec{R}} \cos^4\theta \, d\Omega_\kappa = 4\pi \left\{ F_3(b) + G(b) - \frac{8}{b^2} F_3(b) \right\} \equiv 4\pi b^{-2} f(b) \quad , \tag{B-6}$$

where $F_3(b) = F(b) + 2\,G(b)$ and $f(b) = b^2\,(F_3/b) + G(b) - 8\,F_3(b)$.

Evaluation of $\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos^n\theta \, d\Omega_\kappa d\Omega_{\kappa'}$

The first integral of this type to be treated corresponds to $n = 0$. Separating the $\vec{\kappa}$ and $\vec{\kappa}'$ variables, one obtains

$$\int\int e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \, d\Omega_\kappa \, d\Omega_{\kappa'} = \int e^{\pm i\vec{\kappa}\cdot\vec{R}} \, d\Omega_\kappa \int e^{\pm i\vec{\kappa}'\cdot\vec{R}} \, d\Omega_{\kappa'} \quad .$$

When comparing this expression to the results of equation (B-2), the above integral gives

$$\begin{aligned} \iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \, d\Omega_\kappa \, d\Omega_{\kappa'} &= 2^4\pi^2 \left(\frac{\sin b}{b}\right)\left(\frac{\sin\beta}{\beta}\right) \\ &= 2^4\pi^2 \left\{F(b) - G(b)\right\} \left\{F(\beta) - G(\beta)\right\} \quad . \end{aligned} \tag{B-7}$$

The next integral is given by $\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos\Theta \, d\Omega_\kappa \, d\Omega_{\kappa'}$. Since $\cos\Theta$ is a function of both primed and unprimed variables, one needs to consider this expression as follows: Taking

$$\iint e^{+i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos\Theta \, d\Omega_\kappa \, d\Omega_{\kappa'}$$

$$= \int e^{-i\kappa R\cos\theta} d\Omega_\kappa \int \Big[\cos\theta\cos\theta'$$

$$+ \sin\theta \sin\theta' \cos(\phi-\phi')\Big] e^{-i\kappa' R\cos\theta'} d\Omega_{\kappa'}$$

shows that the integral over $d\phi'$ is simply $\int_0^{2\pi} \cos(\phi-\phi')\, d\phi'$. Using the identity $\cos(\phi-\phi') = \cos\phi\cos\phi' + \sin\phi\sin\phi'$, one readily sees that the integral over ϕ vanishes when integrated from zero to 2π. Thus, the above integral may be evaluated using equation (B-3), as follows:

$$\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos\Theta \, d\Omega_\kappa \, d\Omega_{\kappa'}$$

$$= \int e^{\pm i\kappa R\cos\theta} \cos\theta \, d\Omega_\kappa \int e^{\pm i\kappa' R\cos\theta'} \cos\theta' \, d\Omega_{\kappa'}$$

$$= -2^4\pi^2 \left\{ b\,G(b) \right\} \left\{ \beta\, G(\beta) \right\} \quad . \qquad \text{(B-8)}$$

The next integral is given by $\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos^2\Theta \, d\Omega_\kappa \, d\Omega_{\kappa'}$. Expanding $\cos^2\Theta$, one obtains three terms, one of which contains $\cos(\phi-\phi')$. Eliminating this term, this integral becomes

$$\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos^2 \Theta \, d\Omega_\kappa \, d\Omega_{\kappa'}$$

$$= \iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos^2 \theta \cos^2 \theta' \, d\Omega_\kappa \, d\Omega_{\kappa'}$$

$$+ \iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \sin^2 \theta \sin^2 \theta' \cos^2 (\phi - \phi') \, d\Omega_\kappa \, d\Omega_{\kappa'} \quad .$$

Integrating over $d\phi$, as before and factoring the resulting expressions, the above equation becomes

$$\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos^2 \Theta \, d\Omega_\kappa \, d\Omega_{\kappa'}$$

$$= \int e^{\pm i\vec{\kappa}\cdot\vec{R}} \cos^2 \theta \, d\Omega_\kappa \int e^{\pm i\vec{\kappa}'\cdot\vec{R}} \cos^2 \theta' \, d\Omega_{\kappa'}$$

$$+ 2\pi^2 \int e^{\pm i\vec{\kappa}\cdot\vec{R}} \sin^2 \theta \sin \theta \, d\theta \int e^{\pm i\vec{\kappa}'\cdot\vec{R}} \sin^2 \theta' \sin \theta \, d\theta \quad .$$

Using the identity $\sin^2 \theta = (1 - \cos^2 \theta)$, the second term in the above equation is transformed into integrals over $\cos^n \theta$. Using previous results in equations (B-2) and (B-4), the above becomes

$$\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos^2 \Theta \, d\Omega_\kappa \, d\Omega_{\kappa'}$$

$$= 2^4 \pi^2 \left\{ \left[F(b) + G(b)\right] \left[F(\beta) + G(\beta)\right] + 2\, G(b)\, G(\beta) \right\} \quad . \tag{B-9}$$

Combining equations (B-7) and (B-9), one obtains [2]

$$\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}\,(1+\cos^2\Theta)\,d\Omega_\kappa\,d\Omega_{\kappa'}$$

$$= 2^5\,\pi^2\,\{F(b)\,F(\beta) + 2\,G(b)\,G(\beta)\} \quad .$$

The next integral is given by $\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}\cos^3\Theta\,d\Omega_\kappa\,d\Omega_{\kappa'}$. Expanding $\cos^3\Theta$, one obtains four terms, one of which is independent of $\cos(\phi-\phi')$ and the other three are proportional to $\cos^n(\phi-\phi')$, $n = 1, 2, 3$, respectively. Hence, one needs to evaluate $\int\cos^3(\phi-\phi')\,d\phi\,d\phi'$ by expanding into products of $\sin\phi$ and $\cos\phi$. After doing this and integrating term by term, the answer is zero. Incorporating these simplifications, the term under consideration reduces to

$$\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}}\cos^3\Theta\,d\Omega_\kappa\,d\Omega_{\kappa'}$$

$$= \pi^2\iint e^{\pm i\kappa R\cos\theta}\,e^{\pm i\kappa' R\cos\theta'}\,\sin\theta\,d\theta\,\sin\theta'\,d\theta'$$

$$\times\ \{10\cos^3\theta\cos^3\theta' - 6\cos\theta\cos^3\theta'$$

$$- 6\cos^3\theta\cos\theta' + 6\cos\theta\cos\theta'\} \quad .$$

Using the results obtained in equations (B-3) and (B-5), the above integral reduces to

$$\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos^3\Theta \, d\Omega_{\kappa} \, d\Omega_{\kappa'}$$

$$= (-4\pi^2) \left\{ 10\left[b\,G(b) - \frac{2\,F_3(b)}{b} \right]\left[\beta\,G(\beta) - \frac{2\,F_3(\beta)}{\beta} \right] \right.$$

$$- 6 \left[b\,G(b)\right] \left[\beta\,G(\beta) - \frac{2\,F_3(\beta)}{\beta} \right]$$

$$- 6 \left[b\,G(b) - \frac{2\,F_3(b)}{b} \right] \left[\beta\,G(\beta)\right]$$

$$\left. + 6 \left[b\,G(b)\right] \left[\beta\,G(\beta)\right] \right\}$$

$$= -2^4\,\pi^2 \frac{\left\{\mathcal{F}_2(b)\,\mathcal{F}_2(\beta) + 6\,F_3(b)\,F_3(\beta)\right\}}{(b\beta)} , \qquad \text{(B-10)}$$

where $\mathcal{F}_2(b) = b^2\,G(b) - 2\,F_3(b)$.

Combining equations (B-8) and (B-10), one obtains the following relation:

$$\iint (\cos\Theta + \cos^3\Theta)\, e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \, d\Omega_{\kappa} \, d\Omega_{\kappa'}$$

$$= 2^4\,\pi^2 \left[\left\{ \left[b\,G(b)\right]\left[\beta\,G(\beta)\right] \right\} \right.$$

$$+ \left\{ b\,G(b)\,\beta\,G(\beta) - 2\,b\,G(b)\,\frac{F_3(\beta)}{\beta} \right.$$

$$\left.\left. - \frac{2\,F_3(b)}{b}\,\beta\,G(\beta) + 10\,\frac{F_3(b)}{b}\,\frac{F_3(\beta)}{\beta} \right\} \right] ,$$

$$= -2^5\,\pi^2 \frac{\left[\mathcal{F}(b)\,\mathcal{F}(\beta) + 4\,F_3(b)\,F_3(\beta)\right]}{b\beta} .$$

The next term is given by $\iint e^{\pm i (\overrightarrow{\kappa + \kappa'}) \cdot \vec{R}} \cos^4 \Theta \, d\Omega_\kappa \, d\Omega_{\kappa'}$. Expanding $\cos^4 \Theta$, excluding the terms containing $\cos(\phi - \phi')$ and $\cos^3(\phi - \phi')$, and noting that $\iint \cos^4(\phi - \phi') \, d\phi \, d\phi' = 3/2 \, \pi^2$, the term under consideration factors into the following form:

$$\iint e^{\pm i (\overrightarrow{\kappa + \kappa'}) \cdot \vec{R}} \cos^4 \Theta \, d\Omega_\kappa \, d\Omega_{\kappa'}$$

$$= \frac{\pi^2}{2} \Big[8 \int e^{\pm i \kappa R \cos\theta} \cos^4\theta \sin\theta \, d\theta \int e^{\pm i \kappa' R \cos\theta'} \cos^4\theta' \sin\theta' \, d\theta'$$

$$+ 24 \int e^{\pm i \kappa R \cos\theta} (\cos^2\theta - \cos^4\theta) \sin\theta \, d\theta \int e^{\pm i \kappa' R \cos\theta'} (\cos^2\theta' - \cos^4\theta') \sin\theta' \, d\theta'$$

$$+ 3 \int e^{\pm i \kappa R \cos\theta} (1 - 2\cos^2\theta + \cos^4\theta) \sin\theta \, d\theta \int e^{\pm i \kappa' R \cos\theta'} (1 - 2\cos^2\theta' + \cos^4\theta') \sin\theta' \, d\theta' \Big] \, .$$

Using previous results given in equations (B-2), (B-4), and (B-6), the above integral is given by

$$\iint e^{\pm i (\overrightarrow{\kappa + \kappa'}) \cdot \vec{R}} \cos^4 \Theta \, d\Omega_\kappa \, d\Omega_{\kappa'}$$

$$= \frac{\pi^2}{2} \Bigg[(8)(4) \left\{ F_3(b) + G(b) - \frac{8}{b^2} F_3(b) \right\} \left\{ F_3(\beta) + G(\beta) - \frac{8}{b^2} F_3(\beta) \right\}$$

$$+ (24)(16) \left\{ G(b) - \frac{4 F_3(b)}{b^2} \right\} \left\{ G(\beta) - \frac{4 F_3(\beta)}{\beta^2} \right\}$$

$$+ (3)(16)(16) \left\{ \frac{F_3(b)}{b^2} \right\} \left\{ \frac{F_3(\beta)}{\beta^2} \right\} \Bigg]$$

$$= 2^4 \pi^2 \left[f(b) \, f(\beta) + 12 \, \mathcal{F}_4(b) \, \mathcal{F}_4(\beta) + 24 \, F_3(b) \, F_3(\beta) \right] \quad , \qquad \text{(B-11)}$$

where, $f(b) = b^2 F_4(b) - 8 F_3(b)$ and $\mathcal{F}_4(b) = b^2 G(b) - 4 F_3(b)$. Combining the results of equations (B-9) and (B-11), one obtains the relation

$$\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}') \cdot \vec{R}} (\cos^2 \Theta + \cos^4 \Theta)\, d\Omega_{\kappa}\, d\Omega_{\kappa'}$$

$$= 2^4 \pi^2 \left\{ \left[F_2(b)\ F_2(\beta) + 2\ G(b)\ G(\beta)\right] + \frac{f(b)\ f(\beta) + 12\ \mathcal{F}_4(b)\ \mathcal{F}_4(\beta) + 24\ F_3(b)\ F_3(\beta)}{b^2\ \beta^2} \right\} .$$

Evaluation of $\iint e^{\pm i(\vec{\kappa}-\vec{\kappa}')\cdot \vec{R}} \cos^n \Theta d\Omega_{\kappa} d\Omega_{\kappa'}$

The first term that needs to be evaluated is given by $\iint e^{\pm i(\vec{\kappa}-\vec{\kappa}') \cdot \vec{R}}\, d\Omega_{\kappa}\, d\Omega_{\kappa'}$. Using the previous techniques and definitions, this may be written as

$$\iint e^{\pm i(\vec{\kappa}-\vec{\kappa}') \cdot \vec{R}}\, d\Omega_{\kappa}\, d\Omega_{\kappa'} = \int e^{\pm i \vec{\kappa} \cdot \vec{R}}\, d\Omega_{\kappa} \int e^{\mp i \vec{\kappa}' \cdot \vec{R}}\, d\Omega_{\kappa'}$$

$$= \iint e^{\pm i(\vec{\kappa}+\vec{\kappa}') \cdot \vec{R}}\, d\Omega_{\kappa}\, d\Omega_{\kappa'} \quad . \qquad \text{(B-12)}$$

The next term may be written as

$$\iint e^{\pm i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}} \cos\Theta \, d\Omega_{\kappa} \, d\Omega_{\kappa'}$$

$$= \int e^{\pm i\vec{\kappa}\cdot\vec{R}} \cos\theta \, d\Omega_{\kappa} \int e^{\mp i\vec{\kappa}'\cdot\vec{R}} \cos\theta' \, d\Omega_{\kappa'}$$

$$= +\, 2^4 \pi^2 \left\{ b\,G(b) \right\} \left\{ \beta\, G(\beta) \right\}$$

$$= -\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos\Theta \, d\Omega_{\kappa} \, d\Omega_{\kappa'} \quad . \qquad \text{(B-13)}$$

The next term contains $\cos^2\Theta$ and is evaluated as follows:

$$\iint e^{\pm i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}} \cos^2\Theta \, d\Omega_{\kappa} \, d\Omega_{\kappa'}$$

$$= \int e^{\pm i\vec{\kappa}\cdot\vec{R}} \cos^2\theta \, d\Omega_{\kappa} \int e^{\mp i\vec{\kappa}'\cdot\vec{R}} \cos^2\theta' \, d\Omega_{\kappa'}$$

$$+\, 2\pi^2 \int e^{\pm i\vec{\kappa}\cdot\vec{R}} \sin^2\theta \sin\theta \, d\theta \int e^{\mp i\vec{\kappa}'\cdot\vec{R}} \sin^2\theta' \sin\theta' \, d\theta' \quad .$$

Expressing $\sin^2\theta$ in terms of $(1 - \cos^2\theta)$ and using the results of equations (B-2) and (B-4), one finds that

$$\int\int e^{\pm i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}} \cos^2\Theta \, d\Omega_{\kappa} \, d\Omega_{\kappa'}$$

$$= \int\int e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos^2\Theta \, d\Omega_{\kappa} \, d\Omega_{\kappa'} \quad . \qquad \text{(B-14)}$$

The next expression, when expanded using previous results, gives

$$\iint e^{\pm i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}} \cos^3\Theta \, d\Omega_\kappa \, d\Omega_{\kappa'}$$

$$= \pi^2 \iint e^{\pm i\kappa R\cos\theta} \, e^{\mp i\kappa' R\cos\theta'} \sin\theta \, d\theta \, \sin\theta' \, d\theta'$$

$$\times \left\{ 10\cos^3\theta\cos^3\theta' - 6\cos\theta\cos^3\theta' - 6\cos^3\theta\cos\theta' + 6\cos\theta\cos\theta' \right\} \quad .$$

Using the results of equations (B-3) and (B-5), one sees that the respective integral products are just the negative of the corresponding terms in equation (B-10) hence,

$$\iint e^{\pm i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}} \cos^3\Theta \, d\Omega_\kappa \, d\Omega_{\kappa'} = -\iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos^3\Theta \, d\Omega_\kappa \, d\Omega_{\kappa'} \quad . \tag{B-15}$$

The next term to be considered involves $\cos^4\Theta$. Referring to the equations leading to equation (B-11), one notes that the terms contain $\cos^n\theta$, where $n = 0, 2, 4$. Analysis of equations (B-2), (B-4), and (B-6) shows that all these terms are invariant under sign changes in the exponential factor; hence,

$$\iint e^{\pm i(\vec{\kappa}-\vec{\kappa}')\cdot\vec{R}} \cos^4\Theta \, d\Omega_\kappa \, d\Omega_{\kappa'} = \iint e^{\pm i(\vec{\kappa}+\vec{\kappa}')\cdot\vec{R}} \cos^4\Theta \, d\Omega_\kappa \, d\Omega_{\kappa'} \quad . \tag{B-16}$$

APPENDIX C

PROPAGATION VECTOR INTEGRALS

Introduction

In this appendix, the integrals over β and b ($\kappa R = b$, $\kappa' R = \beta$) necessary in this calculation are evaluated using various techniques employed to obtain the principal value of integral functions. Very few specific references are given since most of the material can be found in standard books on advanced calculus or complex variables. In evaluating integrals of the type considered here, one assumes convergence at infinity in all cases where the integral considered is evaluated over contours which include circular paths at infinity. This requirement is necessary to obtain finite results for this type of problem [1]. This aspect of the calculation could have been treated by including in each integral over $\vec{\kappa}$ and $\vec{\kappa}'$ a convergence factor $e^{-|\gamma|\kappa}$, which would have guaranteed finite results during the various integrations. After the integrations, this factor is removed by letting $|\gamma| = 0$ in the final results. This divergence results when the variation of the electromagnetic field within the atoms is not treated exactly; in fact, in the dipole-dipole approximation $\left(e^{i\vec{\kappa}\cdot\vec{r}} \rightarrow 1\right)$, it is entirely neglected[18]. Casimir and Polder [1] remove this divergence by explicitly introducing the factor $e^{-|\gamma|\kappa}$ in their $\vec{\kappa}$ and $\vec{\kappa}'$ integrals. In this calculation, the addition of this factor would only make things more cumbersome and so it is left out throughout the discussion. Power and Zienau [4] only mention this convergence factor, as is done here, to use the resulting integrals. [See equations (10) and (26) of Reference 4.]

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18. The electromagnetic vector potential is then assumed constant over each atom.

β- Integrals

The first integral to be considered is given by $\int_0^\infty \frac{\beta^2 d\beta \; F(\beta)}{(\beta + b)(\beta - b)}$.

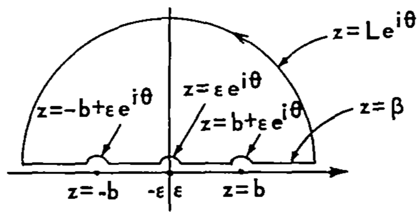
Using the definition for $F(\beta)$ in terms of exponential functions, this integral becomes

$$\int_0^\infty \frac{\beta^2 d\beta \; F(\beta)}{(\beta + b)(\beta - b)} = \int_0^\infty \frac{\beta^2 d\beta}{(\beta + b)(\beta - b)} \left\{ \frac{(\beta^2 + i\beta - 1)e^{i\beta} - (\beta^2 - i\beta - 1)e^{-i\beta}}{2\, i\beta^3} \right\}$$

$$= \int_0^\infty \frac{d\beta(\beta^2 + i\beta - 1)e^{i\beta}}{2i\beta\;(\beta + b)(\beta - b)} - \int_0^\infty \frac{d\beta(\beta^2 - i\beta - 1)e^{-i\beta}}{2i\beta\;(\beta + b)(\beta - b)} .$$

Letting $\beta \to -\beta$ in the second integral, one notes that the integrand changes into the form of the first integral and the limits change from $(+\infty)$ to $(-\infty)$. Interchanging limits, the above two terms may be added to give $\int_{-\infty}^{+\infty} \frac{d\beta(\beta^2 + i\beta - 1)e^{i\beta}}{2i\beta\;(\beta + b)(\beta - b)}$. To obtain the principal value[19] of this integral, one takes the following complex integral:

$$\oint F(z) = \oint \frac{dz\;(z^2 + iz - 1)e^{iz}}{2iz\;(z + b)(z - b)} ,$$



evaluated around the indicated contour. Since no poles are enclosed, the above complex integral vanishes; hence,

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19. The explicit notation P.V. $\int$ will be used only when there is a question as to the value of the integral being considered.

$$\lim_{\substack{\epsilon \to 0 \\ L \to \infty}} \left\{ \int_{-L}^{-b-\epsilon} F(z=\beta)\,dz + \int_{\pi}^{0} F(z=-b+\epsilon e^{i\theta})\,dz + \int_{-b+\epsilon}^{-\epsilon} F(z=\beta)\,dz \right.$$

$$+ \int_{\pi}^{0} F(z=\epsilon e^{i\theta})\,dz + \int_{\epsilon}^{b-\epsilon} F(z=\beta)\,dz + \int_{\pi}^{0} F(z=b+\epsilon e^{i\theta})\,dz$$

$$\left. + \int_{b+\epsilon}^{L} F(z=\beta) + \int_{0}^{\pi} F(z=Le^{i\theta})\,dz \right\} = 0 \quad .$$

Rearranging terms and assuming convergence at $L \to \infty$, one obtains the principal value (P.V.) of the desired integral by transposing terms. Hence,

$$\text{P.V.} \int_{-\infty}^{+\infty} dz\, F(z=\beta) \equiv \lim_{\substack{\epsilon \to 0 \\ L \to \infty}} \left\{ \int_{-L}^{-b-\epsilon} F(z)\,dz + \int_{-b+\epsilon}^{-\epsilon} F(z)\,dz \right.$$

$$\left. + \int_{\epsilon}^{b-\epsilon} F(z)\,dz + \int_{b+\epsilon}^{L} F(z)\,dz \right\}$$

$$= \lim_{\epsilon \to 0} \left\{ \int_{0}^{\pi} F(z=-b+\epsilon e^{i\theta})\,dz + \int_{0}^{\pi} F(z=\epsilon e^{i\theta})\,dz \right.$$

$$\left. + \int_{0}^{\pi} F(z=b+\epsilon e^{i\theta})\,dz \right\} \quad .$$

Substituting for z in each of the above integrals and interchanging limiting and integral operations, the above becomes

$$\text{P.V.} \int_{-\infty}^{+\infty} dz\, F(z=\beta) = \left\{ \frac{\pi}{2b^2} \right\} + \frac{\pi i b}{2} \left\{ \frac{1}{2ib^3} \left[(b^2+ib-1)e^{ib} \right.\right.$$

$$\left.\left. + (b^2-ib-1)e^{-ib} \right] \right\} \quad .$$

Hence,

$$\int_0^{\infty} \frac{\beta^2 d\beta \, F(\beta)}{(\beta + b)(\beta - b)} = \left\{ \frac{\pi}{2b^2} + \frac{i\pi}{2} \, b \, F^+(b) \right\} \quad . \tag{C-1}$$

The next integral that needs to be considered is similar to the one just evaluated, with only $F(\beta)$ replaced by $G(\beta)$. Following a similar procedure, this integral is given by

$$\int_0^{\infty} \frac{\beta^2 d\beta \, G(\beta)}{(\beta + b)(\beta - b)} = \left\{ \frac{\pi}{2b^2} + \frac{i\pi}{2} \, b \, G^+(b) \right\} \quad . \tag{C-2}$$

where

$$G^+(b) = \frac{1}{b^3} \left[\frac{(ib - 1)e^{ib}}{2i} + \frac{(-ib - 1)e^{-ib}}{2i} \right] \quad .$$

The next integral expression is $\int \beta \, d\beta \, F(\beta) \left(\frac{1}{b + \beta} + \frac{1}{\beta - b} \right)$. Rearranging the factors and fractions, the above quantity can be written as $2 \int \frac{\beta^2 d\beta \, F(\beta)}{(\beta + b)(\beta - b)}$. This integral is the same as the one considered previously; hence, the result is obtained directly, using equation (C-1). The integral under consideration may also be evaluated by taking $\int \beta \, d\beta \, F(\beta) \left(\frac{1}{b + \beta} + \frac{1}{\beta - b} \right)$ and separating $F(\beta)$ as $F(\beta) = \frac{I(\beta)}{\beta^3}$, where $I(\beta) = (\beta^2 \sin \beta + \beta \cos - \sin \beta)$. Hence, this integral can be written as $\int d\beta \, I(\beta) \frac{1}{\beta^2} \left(\frac{1}{b + \beta} + \frac{1}{\beta - b} \right)$. Expanding the fraction, this integral becomes $\int d\beta \, I(\beta) \left\{ -\frac{2}{b^2 \beta} + \frac{1}{b^2} \left(\frac{1}{b + \beta} + \frac{1}{\beta - b} \right) \right\}$. The last step may be checked by simply collecting terms under a common denominator on both fractions. Hence, one needs to evaluate three integrals given by

$$- \frac{2}{b^2} \int_0^\infty \frac{I(\beta)\,d\beta}{\beta} + \frac{1}{b^2} \int_0^\infty \frac{I(\beta)\,d\beta}{(b+\beta)} + \frac{1}{b^2} \int_0^\infty \frac{I(\beta)\,d\beta}{(\beta - b)}$$

. Since $I(\beta) = \left\{ \frac{(\beta^2 + i\beta - 1)e^{i\beta}}{2i} - \frac{(\beta^2 - i\beta - 1)e^{-i\beta}}{2i} \right\}$, the first integral may be separated into two parts as follows:

$$\int_0^\infty \frac{(\beta^2 + i\beta - 1)e^{i\beta}}{2i\beta}\, d\beta - \int \frac{(\beta^2 - i\beta - 1)e^{-i\beta}}{2i\beta}\, d\beta \quad .$$

Letting $\beta \to -\beta$ in the second term and interchanging the resulting limits of integration, the two parts combine into $\int_{-\infty}^{+\infty} \frac{(\beta^2 + i\beta - 1)e^{i\beta}}{2i\beta}\, d\beta$. Performing the same operations on $\int_0^\infty \frac{I(\beta)\,d\beta}{(\beta - b)}$ and using the fact that $I(\beta) = -I(-\beta)$, one can combine the remaining two integrals into $\frac{1}{b^2} \int_{-\infty}^{\infty} \frac{I(\beta)\,d\beta}{(b+\beta)}$. Thus, the integral under consideration becomes

$$\int_0^\infty \beta\, d\beta\, F(\beta) \left(\frac{1}{b+\beta} + \frac{1}{\beta - b} \right) = - \frac{2}{b^2} \int_{-\infty}^{+\infty} \frac{(\beta^2 + i\beta - 1)e^{i\beta}}{2i\beta}\, d\beta$$

$$+ \frac{1}{b^2} \int_{-\infty}^{\infty} \frac{I(\beta)\,d\beta}{(b+\beta)} \; , \quad F(\beta) = \frac{I(\beta)}{\beta^3} \quad .$$

Substituting for $1/\beta$ and $1/(b+\beta)$ their respective principal value [20, 21] defined as

$$\frac{P}{\beta} \equiv \zeta(\beta) + i\pi\delta(\beta) \; , \quad \frac{P}{(\beta + b)} \equiv \zeta\left[\beta - (-b)\right] + i\pi\delta\left[\beta - (-b)\right] \; ,$$

where

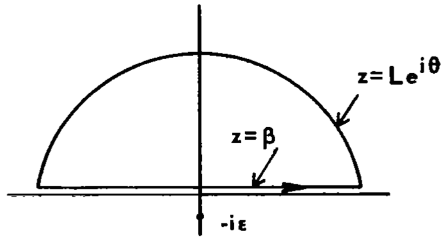
$$\zeta(\beta) \equiv \lim_{\epsilon\to 0}\left(\frac{1}{\beta + i\epsilon}\right), \quad \delta(\beta) \equiv \lim_{\epsilon\to 0} \frac{\epsilon}{\pi(\beta^2+\epsilon^2)} ,$$

then one can evaluate the integrals by using the rules [20] for integrating over the $\zeta(\beta)$ and $\delta(\beta)$ functions. Taking the first integral, one obtains

$$\int_{-\infty}^{\infty} \frac{(\beta^2 + i\beta - 1)e^{i\beta}}{2i\beta}\, d\beta$$

$$= \int_{-\infty}^{\infty} d\beta \frac{(\beta^2 + i\beta - 1)e^{i\beta}}{2i}\, \zeta(\beta)$$

$$+ i\pi \int_{-\infty}^{\infty} d\beta \frac{(\beta^2 + i\beta - 1)e^{i\beta}}{2i}\, \delta(\beta)$$

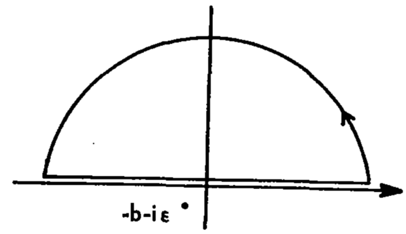


$$= \lim_{\epsilon\to 0} \oint \frac{(z^2 + iz - 1)e^{iz}}{2i\,(z + i\epsilon)} + i\pi\left(-\frac{1}{2i}\right) = -\left(\frac{\pi}{2}\right) ,$$

where the first integral doesn't contribute since no poles are enclosed by the contour[20]. The next integral is evaluated as follows:

20. Note that in this case one must use the requirement of convergence at infinity obtained by the implied convergence factor $e^{-|\gamma|z}$.

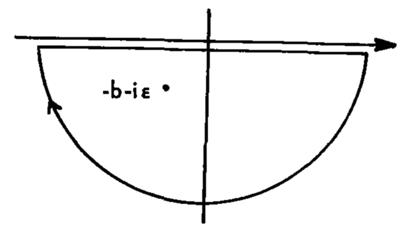
$$\int_{-\infty}^{\infty} \frac{I(\beta)\,d\beta}{(b+\beta)}$$



$$= \int_{-\infty}^{\infty} \frac{(\beta^2 + i\beta - 1)e^{i\beta}}{2i} \zeta\left[\beta - (-b)\right]$$

$$- \int_{-\infty}^{\infty} \frac{(\beta^2 - i\beta - 1)e^{-i\beta}}{2i} \zeta\left[\beta - (-b)\right]$$

$$+ i\pi \int_{-\infty}^{\infty} I(\beta)\,d\beta\, \delta\left[\beta - (-b)\right]$$



$$= \lim_{\epsilon \to 0} \oint \frac{(z^2 + iz - 1)e^{iz}}{2i\,(\beta + b + i\epsilon)}\,dz$$

$$- \lim_{\epsilon \to 0} \oint \frac{(z^2 - iz - 1)e^{-iz}}{2i\,(\beta + b + i\epsilon)}\,dz + i\pi \int_{-\infty}^{\infty} I(\beta)\,d\beta\,\delta\left[\beta - (-b)\right] \quad .$$

Since no poles are included in the contour corresponding to the first integral above, its value is zero. In the second integral, the contour must be taken over the negative half plane; hence, a pole is included within the contour. Thus, the value of this integral is obtained using the Residue Theorem. Integrating over the δ-function, the above expression becomes

$$\int_{-\infty}^{\infty} \frac{I(\beta)\,d\beta}{(b+\beta)} = \pi \left[(b^2 + ib - 1)\,e^{ib} \right] + i\pi\, I(-b) \quad .$$

The integral containing the δ function is given by

$$i\pi\, I(-b) = i\pi \left\{ \frac{(b^2 - ib - 1)e^{-ib}}{2i} - \frac{(b^2 + ib - 1)e^{ib}}{2i} \right\} \quad .$$

Noting that the terms containing e^{ib} add, one finally obtains

$$\int_{-\infty}^{\infty} \frac{I(\beta)\,d\beta}{(b+\beta)} = \frac{\pi}{2}\left[(b^2 + ib - 1)e^{ib} + (b^2 - ib - 1)e^{-ib}\right] .$$

Collecting terms, the β integral under consideration is

$$\int_{-\infty}^{\infty} \beta\,d\beta\, F(\beta)\left(\frac{1}{b+\beta} + \frac{1}{\beta - b}\right) = -\frac{2}{b^2}\left(-\frac{\pi}{2}\right) + \frac{\pi}{2b^2}\left[(b^2 + ib - 1)e^{ib} + (b^2 - ib - 1)e^{-ib}\right]$$

$$= \left\{\frac{\pi}{b^2} + i\pi b\, F^{+}(b)\right\} .$$

Combining the fractions on the left hand side of the above equation, one obtains $2\int \frac{\beta\,d\beta\, F(\beta)}{(\beta + b)(\beta - b)}$. Dividing by the factor of 2, complete agreement with equation (C-1) is obtained. The reason for including this alternate method of handling this type of integrals is to provide a means of checking some of the results and because sometimes this method is easier to apply.

The next integral is given by

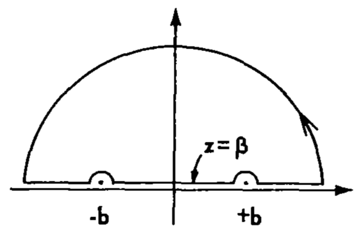
$$\int \beta\,d\beta\, F(\beta)\frac{(b^2 + \beta^2)}{(b+\beta)} = \int \frac{\beta\,d\beta\, F(\beta)}{(b+\beta)} + \int \frac{\beta^2\,d\beta\, F(\beta)}{(b+\beta)} .$$

Multiplying by $(\beta - b)$ on the numerator and denominator and interchanging b and β on two of the terms, one obtains

$$\int \beta\,d\beta\, F(\beta)\frac{(b^2 + \beta^2)}{(b+\beta)} = 2\int \frac{\beta^2\,d\beta\, F(\beta)}{(b+\beta)(\beta - b)} + 2\int \frac{\beta^4\,d\beta\, F(\beta)}{(b+\beta)(\beta - b)} .$$

The first of these integrals has already been evaluated; the other integral is evaluated as follows:

$$\int_0^\infty \frac{\beta^4 d\beta\ F(\beta)}{(\beta + b)(\beta - b)}$$



$$= \int_0^\infty \frac{\beta^4 d\beta}{(\beta + b)(\beta - b)} \frac{1}{\beta^3} \left(\frac{\beta^2 + i\beta - 1}{2i} \right) e^{i\beta}$$

$$- \int_0^\infty \frac{\beta^4 d\beta\ F(\beta)}{(\beta + b)(\beta - b)} \frac{1}{\beta^3} \left(\frac{\beta^2 - i\beta - 1}{2i} \right) e^{-i\beta}$$

$$= \int_{-\infty}^\infty \frac{\beta\, d\beta\, (\beta^2 + i\beta - 1) e^{i\beta}}{(\beta + b)(\beta - b)} = \lim_{\epsilon \to 0} \left[\int_0^\pi F(z = -b + \epsilon e^{i\theta})\, dz \right.$$

$$\left. + \int_0^\pi F(z = b + \epsilon e^{i\theta})\, dz \right] = \frac{\pi i}{2} b^3 F^+(b) \quad . \tag{C-3}$$

Combining terms, one obtains

$$\int b\, db\, F(b) \int \beta\, d\beta\, F(\beta) \left(\frac{b^2 + \beta^2}{b + \beta} \right)$$

$$= 2 \int b^3 db\, F(b) \left\{ \frac{\pi}{2b^2} + \frac{i\pi}{2} b\, F^+(b) \right\} + 2 \int b\, db\, F(b) \left\{ \frac{\pi i}{2} b^3 F^+(b) \right\}$$

$$= \left\{ \pi \int b\, db\, F(b) + 2 i \pi \int b^4 db\, F(b)\, F^+(b) \right\} \quad .$$

The integral corresponding to the above, but containing $G(\beta)$ instead of $F(\beta)$, is obtained directly from the above results.

The next integrals of interest are given by

$$\int b\,db \int \beta\, d\beta \left(\frac{1}{b+\beta}\right) \left[\mathcal{F}(b)\ \mathcal{F}(\beta) + 4\ F_3(b)\ F_3(\beta)\right] \quad .$$

Multiplying by' $(b - \beta)$ in the numerator and denominator of the above expression and recombining as before, the above expression becomes

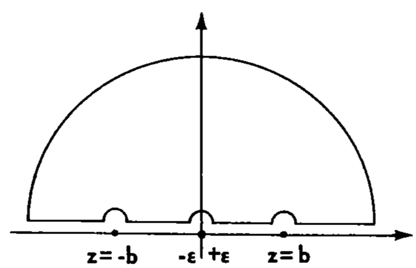
$$2 \int b\,db \int \frac{\beta^2 d\beta \left\{ \mathcal{F}(b)\ \mathcal{F}(\beta) + 4\ F_3(b)\ F_3(\beta) \right\}}{(b+\beta)(\beta - b)}$$

$$= 2 \int b\,db\ \mathcal{F}(b) \int \frac{\beta^2 d\beta\ \mathcal{F}(\beta)}{(b+\beta)(\beta - b)} + 8 \int b\,db\ F_3(b) \int \frac{\beta^2 d\beta\ F_3(\beta)}{(b+\beta)(\beta - b)} \ .$$

The β integrals are of the same form as the ones considered previously with only $\mathcal{F}(\beta)$ and $F_3(\beta)$ replacing $F(\beta)$ and $G(\beta)$. Following the steps leading to equation (C-1), one notes that since $\mathcal{F}(\beta)$ and $F_3(\beta)$ have different coefficients than $F(\beta)$, only the residue at $\beta = 0$ changes value. This can be seen by considering these integrals as follows:

$$\int_0^\infty \frac{\beta^2 d\beta\ \mathcal{F}(\beta)}{(b+\beta)(\beta - b)}$$

$$= \int_{-\infty}^{\infty} \frac{d\beta\,(i\beta^3 - 2\beta^2 - 3i\beta + 3)\,e^{i\beta}}{2i\beta(\beta + b)(\beta - b)}$$



$$= \lim_{\epsilon \to 0} \left[\int_0^\pi F(z = -b + \epsilon e^{i\theta})\, dz \right.$$

$$\left. + \int_0^\pi F(z = \epsilon e^{i\theta})\, dz + \int_0^\pi F(z = b + \epsilon e^{i\theta})\, dz \right] \quad ,$$

$$\int_0^\infty \frac{\beta^2 d\beta\ \mathcal{F}(\beta)}{(b+\beta)(\beta-b)}$$

$$= \frac{\pi i}{2b^2}\left[\frac{(-ib^3 - 2b^2 + 3ib + 3)e^{-ib}}{2i}\right] + \frac{3\pi}{(-2b^2)}$$

$$+ \frac{\pi i}{2b^2}\left[\frac{(ib^3 - 2b^2 - 3ib + 3)e^{ib}}{2i}\right] = \left\{-\frac{(3\pi)}{2b^2} + \frac{i\pi}{2}\ b\,\mathcal{F}^-(b)\right\} \quad ;$$

$$\int_0^\infty \frac{\beta^2 d\beta\ F_3(\beta)}{(\beta+b)(\beta-b)} = \int_{-\infty}^\infty \frac{d\beta(\beta^2 + 3i\beta - 3)e^{ib}}{(\beta+b)(\beta-b)} = \left\{+\left(\frac{3\pi}{2b^2}\right) + \frac{i\pi}{2}\ b\ F_3^+(b)\right\} \quad . \tag{C-4}$$

Note that the sign change in the $(3\pi/2b^2)$ term is due to the corresponding sign change in the constant factors of the β polynomials in $\mathcal{F}(\beta)$ and $F_3(\beta)$ respectively. A similar integral occurs with exactly the same form as the above term, being considered with only $\mathcal{F}(\beta)$ replaced by $\mathcal{F}_2(\beta)$. Since $\mathcal{F}_2(\beta) = \beta^2\, G(\beta) - 2\, F_3(\beta)$, which when expanded gives

$$\frac{1}{\beta^3}\left[\frac{(i\beta^3 - 3\beta^2 - 6i\beta + 6)e^{i\beta}}{2i} + \frac{(i\beta^3 + 3\beta^2 - 6i\beta - 6)e^{-i\beta}}{2i}\right] \quad ,$$

and noting that the residue at the origin contains the constant factor in the polynomial factor in β, the result for this integral is

$$\int_0^\infty \frac{\beta^2 d\beta\ \mathcal{F}_2(\beta)}{(\beta+b)(\beta-b)} = \left[-\frac{(2)(3\pi)}{2b^2} + \frac{i\pi}{2}\mathcal{F}_2^-(b)\right] \quad .$$

The next group of β integrals are contained in the term

$$\int b\,db \int \frac{\beta\, d\beta}{(b+\beta)}\ (b^2+\beta^2)^2\ \{F(b)\ F(\beta) + 2\ G(b)\ G(\beta)\} \quad .$$

Expanding these factors and rearranging terms as before, the preceding expression becomes

$$\left\{ 2 \int b^5 db \int \frac{\beta^2 d\beta \{F(b) F(\beta) + 2 G(b) G(\beta)\}}{(b+\beta)(\beta - b)} \right.$$

$$+ 4 \int b^3 db \int \frac{\beta^4 d\beta \{F(b) F(\beta) + 2 G(b) G(\beta)\}}{(b+\beta)(\beta - b)}$$

$$\left. + 2 \int b db \int \frac{\beta^6 d\beta \{F(b) F(\beta) + 2 G(b) G(\beta)\}}{(b+\beta)(\beta - b)} \right\}$$

Analysis of the above terms shows that only the last term needs to be evaluated. Using the same procedure as before,

$$\int_0^\infty \frac{\beta^6 d\beta \, F(\beta)}{(\beta + b)(\beta - b)} = \int_{-\infty}^\infty \frac{\beta^3 d\beta (\beta^2 + i\beta - 1) e^{i\beta}}{2i \, (\beta + b)(\beta - b)} = \left\{ \frac{i\pi}{2} b^5 F^+(b) \right\} \quad . \quad \text{(C-5)}$$

The next integral appears in the term given by

$$\int b db \int \frac{\beta d\beta}{(b+\beta)} (b^2 + \beta^2) \left\{ \mathcal{F}(b) \mathcal{F}(\beta) + 4 F_3(b) F_3(\beta) \right\}$$

$$= 2 \int b^3 db \int \frac{\beta^2 d\beta \{\mathcal{F}(b) \mathcal{F}(\beta) + 4 F_3(b) F_3(\beta)\}}{(b+\beta)(\beta - b)}$$

$$+ 2 \int b db \int \frac{\beta^4 d\beta \{\mathcal{F}(b) \mathcal{F}(\beta) + 4 F_3(b) F_3(\beta)\}}{(\beta + b)(\beta - b)} \quad .$$

The first integral above has been evaluated previously. The second integral is obtained as follows:

$$\int_0^\infty \frac{\beta^4 \, d\beta \, \mathcal{F}(\beta)}{(\beta + b)(\beta - b)}$$

$$= \lim_{\epsilon \to 0} \left[\int_0^\pi F(z = -b + \epsilon e^{i\theta}) \, dz + \int_0^\pi F(z = b + \epsilon e^{i\theta}) \, dz \right] = \frac{i\pi}{2} b^3 \mathcal{F}^-(b)$$

Similar operations are used to obtain

$$\int_0^\infty \frac{\beta^4 \, d\beta \, F_3(\beta)}{(\beta + b)(\beta - b)} = \left\{ \frac{i\pi}{2} b^3 F_3^+(b) \right\} \quad . \tag{C-6}$$

The next integral group is found in the term

$$\int b \, db \int \frac{\beta \, d\beta}{(b + \beta)} \left\{ b^2 \beta^2 \left(\left[F_2(b) \; F_2(\beta) + 2 \, G(b) \; G(\beta) \right] \right. \right.$$

$$+ \frac{1}{b^2 \beta^2} \left[f(b) \; f(\beta) + 12 \, \mathcal{F}_4(b) \; \mathcal{F}_4(\beta) \right.$$

$$\left. \left. \left. + 24 \, F_3(b) \; F_3(\beta) \right] \right) \right\}$$

$$= 2 \int b^3 \, db \int \frac{\beta^4 \, d\beta}{(b + \beta)(\beta - b)} \left\{ F_2(b) \; F_2(\beta) + 2 \, G(b) \; G(\beta) \right\}$$

$$+ 2 \int b \, db \int \frac{\beta^2 \, d\beta}{(\beta + b)(\beta - b)}$$

$$\times \left\{ f(b) \; f(\beta) + 12 \, \mathcal{F}_4(b) \; \mathcal{F}_4(\beta) + 24 \, F_3(b) \; F_3(\beta) \right\} \quad .$$

Using the fact that

$$F_2(\beta) = \frac{1}{\beta^3}\left[\frac{(\beta^2 + 2i\beta - 2)e^{i\beta}}{2i} - \frac{(\beta^2 - 2i\beta - 2)e^{-i\beta}}{2i}\right] ,$$

$$f(\beta) = \frac{1}{\beta^3}\left[\frac{(\beta^4 + 4i\beta^3 - 12\beta^2 + 24i\beta + 24)e^{i\beta}}{2i}\right.$$

$$\left. - \frac{(\beta^4 - 4i\beta^3 - 12\beta^2 + 24i\beta + 24)e^{-i\beta}}{2i}\right] ,$$

$$\mathcal{F}_4(\beta) = \frac{1}{\beta^3}\left[\frac{(i\beta^3 - 5\beta^2 - 12i\beta + 12)e^{i\beta}}{2i} + \frac{(i\beta^3 - 5\beta^2 - 12i\beta - 12)e^{-i\beta}}{2i}\right] ,$$

one can write the results for the above integrals in the order in which they appear:

$$2\int b^3\,db\left[F_2(b)\left\{\frac{i\pi}{2}\,b^3\,F_2^+(b)\right\} + 2\,G(b)\left\{\frac{i\pi}{2}\,b^3\,G^+(b)\right\}\right] ,$$

$$+ 2\int b\,db\left[f(b)\left\{-\frac{24\pi}{2b^2} + \frac{i\pi}{2}\,b\,f^+(b)\right\}\right] ,$$

$$+ 2\int b\,db\left[12\,\mathcal{F}_4(b)\left\{-\frac{(12)\pi}{2b^2} + \frac{i\pi}{2}\,b\,\mathcal{F}_4^-(b)\right\}\right] ,$$

$$+ 2\int b\,db\left[24\,F_3(b)\left\{\frac{(3\pi)}{2b^2} + \frac{i\pi}{2}\,b\,F_3^+(b)\right\}\right] .$$

Integration and Transformation of b-Integrals

The b-integrals resulting from the β integrations are considered in this section. In general, two types of integrals are considered. In some cases the integral's principal value is obtained; whereas in other cases, the integral is simply transformed into another integral expression. This behavior results from the fact that the evaluation of the b-integrals in closed form is not possible [22]. The most one can do is express quantities in terms of sine and cosine integrals defined by

$$S_i(x) = \int_0^x \frac{\sin b}{b}\, db \quad , \quad C_i(x) = \int_\infty^x \frac{\cos b}{b}\, db \quad .$$

The principal value of the first integral to be considered is obtained as follows: Taking

$$\int_0^\infty \frac{db}{ab^3}\left[\frac{(b^2+3\,i\,b-3)e^{i\,b}}{2i} - \frac{(b^2-3\,i\,b-3)e^{-i\,b}}{2i}\right] ,$$

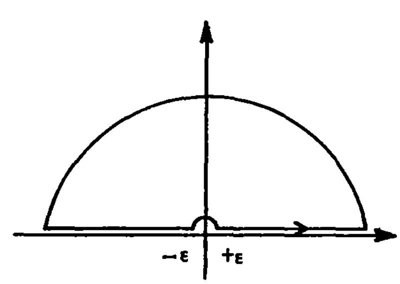
and letting $b \rightarrow -b$ in the second term, the above expression becomes

$$\int_{-\infty}^\infty \frac{db}{ab^3}\, \frac{(b^2+3\,i\,b-3)e^{i\,b}}{2\,i} \quad .$$

Using the contour indicated, this integral becomes

$$\int_{-\infty}^\infty \frac{db}{ab^3}\, \frac{(b^2+3\,i\,b-3)e^{i\,b}}{2\,i}$$

$$= \lim_{\epsilon\to 0}\left[\int_0^\pi F(z=\epsilon e^{i\theta})\,dz\right] \quad .$$



Using the L' Hospital rule in carrying out the limiting operations, the principal value of this integral is

$$\int_{-\infty}^{\infty} \frac{db}{ab^3} \frac{(b^2 + 3ib - 3)e^{ib}}{2i} = \left(-\frac{\pi}{4a}\right) .$$

A similar procedure is used to evaluate the next integral, given by

$$\int_0^{\infty} \frac{db}{2ab^3} \left[\frac{(b^4 + 2ib^3 - 5b^2 - 6ib + 3)e^{2ib}}{2i} - \frac{(b^4 - 2ib^3 - 5b^2 + 6ib + 3)e^{-2ib}}{2i} \right]$$

$$= \int_{-\infty}^{\infty} \frac{db}{2ab^3} \frac{(b^4 + 2ib^3 - 5b^2 - 6ib + 3)e^{2ib}}{2i}$$

$$= \int_0^{\pi} \frac{d\theta}{4a} \left[-5 + 12 + (3i)(2i)\right] = \left(\frac{\pi}{4a}\right)$$

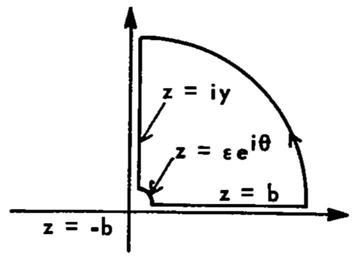
The next integral is given by

$$\int_0^{\infty} \frac{db}{2ab(a+b)^2} \left\{ \frac{(b^4 + 2ib^3 - 5b^2 - 6ib + 3)e^{2ib}}{2i} - \frac{(b^4 - 2ib^3 - 5b^2 + 6ib + 3)e^{-2ib}}{2i} \right\} .$$

Since the two parts of the above expression cannot be combined in the manner used before, one evaluates each of the above terms by considering the complex integral

$$\oint F(z)\, dz$$

$$= \oint \frac{dz}{az(a+z)^2} \left\{ \frac{(z^4 + 2iz - 5z^2 - 6iz + 3)e^{iz}}{2i} \right\}$$



integrated around the indicated contour [23]. Since no poles are enclosed, this integral is given by

$$\oint F(z)dz = \lim_{\substack{\epsilon \to 0 \\ L \to \infty}} \left[\int_{\epsilon}^{L} F(z=b)\,dz + \int_{0}^{\pi/2} F(z = Le^{i\theta})\,dz \right.$$

$$\left. + \int_{iL}^{i\epsilon} F(z=iy)\,dz + \int_{\pi/2}^{0} F(z = \epsilon e^{i\theta})\,dz \right] = 0 \quad .$$

Making use of the convergence at infinity requirement the following is obtained:

$$\lim_{\substack{\epsilon \to 0 \\ L \to \infty}} \int_{\epsilon}^{L} F(z=b)\,dz = \lim_{\substack{\epsilon \to 0 \\ L \to \infty}} \left\{ \int_{0}^{\pi/2} F(z = \epsilon e^{i\theta})\,dz + \int_{i\epsilon}^{iL} F(z=iy)\,dz \right\} \quad .$$

The left-hand side of the above equation is just the principal value of the integral under consideration; hence,

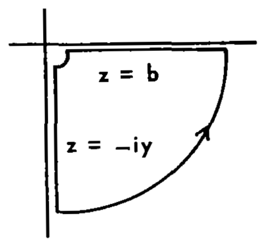
$$\int_0^\infty \frac{db}{2ab(a+b)^2} \left\{ \frac{(b^4+2ib^3-5b^2-6ib+3)e^{+2ib}}{2i} \right\}$$

$$= \left(\frac{3\pi}{8a^3}\right) + \lim_{\substack{\epsilon \to 0 \\ L \to \infty}} \int_{i\epsilon = iy}^{iL = iy} \frac{i\,dy}{a(iy)(a+iy)^2} - \frac{(y^4+2y^3+5y^2+6y+3)e^{-2y}}{2i}$$

$$= \left(\frac{3\pi}{8a^3}\right) + \int_0^\infty \frac{dy}{4a(iy)(a+iy)^2}\,(y^4+2y^3+5y^2+6y+3)e^{-2y} \quad .$$

The term containing the e^{-2ib} is evaluated in the same manner, but the corresponding complex integral $\oint F(z)dz$ is evaluated, using the indicated contour:

$$-\int_0^\infty \frac{db}{2ab(a+b)^2} \left\{ \frac{(b^4-2ib^3-5b^2+6ib+3)e^{-2ib}}{2i} \right\}$$



$$= \left(\frac{3\pi}{8a^3}\right)$$

$$-\int_0^\infty \frac{dy}{4(iy)(a-iy)^2}\,(y^4+2y^3+5y^2+6y+3)e^{-2y} \quad .$$

Combining the above results, the integral being considered equals

$$\left(\frac{3\pi}{4a^3}\right) + \int_0^\infty \frac{dy\{(a-iy)^2-(a+iy)^2\}}{4a(iy)(a^2+y^2)^2} \times \{y^4+2y^3+5y^2+6y+3\}\,e^{-2y} \quad .$$

Rearranging factors, one finally obtains

$$\int_0^\infty \frac{db}{2ab(a+b)^2}\left\{\frac{(b^4+2ib^3-5b^2-6ib+3)e^{2ib}}{2i} - \frac{(b^4-2ib^3-5b^2+6ib+3)e^{-2ib}}{2i}\right\}$$

$$= \left(\frac{3\pi}{4a^3}\right) - \int_0^\infty \frac{dy}{(a^2+y^2)^2}\left\{y^4+2y^3+5y^2+6y+3\right\}e^{-2y} \quad .$$

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